PETROLEUM ASSOCIATION FOR CONSERVATION OF THE CANADIAN ENVIRONMENT
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PACE Report No. 87-2

SAMPLING AND ANALYSIS OF REFINERY EFFLUENTS TO ASSESS VARIATIONS IN TRACE CONTAMINANT CONCENTRATIONS

"Working for a Better Environment"

SAMPLING AND ANALYSIS OF REFINERY EFFLUENTS TO ASSESS VARIATIONS IN TRACE CONTAMINANT CONCENTRATIONS

PACE REPORT NO. 87-2

Prepared for

Petroleum Association for Conservation
of the Canadian Environment (PACE)

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in conjunction with

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by

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NOTICE

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PREFACE

This study was conducted in fulfillment of the preregulation monitoring requirements under Ontario's Municipal Industrial Strategy for Abatement program for the petroleum sector. The project scope was developed in consultation between government and industry. The objectives were to provide data to assist in the development of an effective and workable Regulation. A joint steering committee, comprised of representatives of the Ontario Ministry of the Environment, the Wastewater Technology Centre (Environment Canada) and the Ontario Petroleum Association, managed the project. All conclusions and findings of the report are accepted as valid.

EXECUTIVE SUMMARY

The investigation, which was undertaken on behalf of PACE and in conjunction with the Ontario Petroleum Association, the Ontario Ministry of the Environment and Environment Canada, was aimed at defining the capability of petroleum refinery biological treatment processes to effect trace contaminant removal and to assess the variability of effluent quality.

A comprehensive sampling program was carried out at two Ontario petroleum refineries, the Esso Petroleum Canada Refinery in Sarnia and the Petro-Canada Trafalgar Refinery in Oakville. Six-hour flow-proportioned composite samples of the influent and effluent from the biological treatment plants at each refinery were collected on six occasions over a two-week period. During the sampling periods, biological treatment system operating conditions and key refinery operating conditions were documented. The analytical program focussed on conventional contaminants, metals, selected volatile aromatic compounds and polynuclear aromatic hydrocarbons. A comprehensive quality assurance program was conducted in conjunction with the sampling and analytical components of the investigation.

The biological treatment plants at both refineries were demonstrated to be consistently capable of highly efficient removal of trace organic contaminants. The only trace organic compounds which were detected in more than fifty percent of the effluents from the biological treatment plants from both refineries were phthalate esters. These phthalate esters, which are common plasticizers, were also found in field blank samples and have been consistently reported in all studies characterizing trace organic contaminants in municipal and industrial wastewater. Their presence in the refinery effluent samples may be associated with laboratory or field contamination. Volatile aromatic compounds, including benzene and xylenes, were identified up to 50 percent of the time at near detection limit concentrations in Esso Refinery effluents but were not detected in effluents from the Petro-Canada Refinery. The polynuclear aromatic hydrocarbons (PAHs) present in the influent to both plants were substantially removed. No PAHs were detected in any Esso Refinery effluent sample. At Petro-Canada Refinery, only two substituted PAH compounds (dimethyl and trimethyl naphthalene) were detected in 33 percent of the effluent samples.

Effluent quality was similar at both refineries with respect to trace organic contaminants despite significant difference in influent quality, refinery size and complexity, and biological treatment plant design and operation. Differences in effluent quality at the two refineries was apparent in the concentrations of conventional contaminants; total suspended solids, phenols, TKN and ammonia nitrogen. The Esso Refinery treatment facility, which was operated at an elevated solids retention time (SRT) and was nitrifying, produced an effluent containing lower phenol concentrations than the Petro-Canada Refinery treatment facility which treated influent phenol concentrations an order of magnitude higher, had a lower SRT and was not nitrifying.

The results produced from this monitoring program were consistent with those reported in previous studies of petroleum refinery effluents. In general, fewer trace organic compounds were detected in the present study than in previous studies. Because of the low concentrations of trace contaminants in the treated effluents and the lack of variability in effluent quality, no relationship between refinery or treatment plant operation and trace contaminant removal was identified and no surrogate parameter indicative of trace contaminant concentration in the effluent could be defined. Validation of a surrogate relationship would likely require higher than normal effluent concentrations of conventional contaminants. Further study for a surrogate relationship in a full-scale plant is not warranted.

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1.0 INTRODUCTION AND STUDY OBJECTIVES

Between 1979 and the present, the Petroleum Association for Conservation of the Canadian Environment (PACE) sponsored several major investigations aimed at defining the fate of trace contaminants in petroleum refinery effluents. These investigations characterized the trace substances (organic and inorganic) present in intake water streams, untreated process wastewaters and refinery effluents, attempted to define the fate of organic trace contaminants within the refinery wastewater treatment plant and assessed the variability of trace organic substances in the effluent from one refinery.

On behalf of PACE, in conjunction with the Ontario Petroleum Association (OPA), the Ontario Ministry of the Environment (MOE) and Environment Canada, CANVIRO Consultants undertook the present study to determine the relationship between biological treatment process operating condition and the ability of the process to effect trace contaminant removal. The objectives of this study were threefold:

(i) to determine the relationship between trace contaminant concentrations, biotreatment plant operating conditions (conventional contaminants loading, SRT, HRT, DO concentrations, etc.) and refinery operation (crude throughput, shutdown and upset) for two refineries;

(ii) to provide additional data to allow assessment of the practicability of selecting a surrogate parameter as a measure of trace contaminant removal performance; and

(iii) to validate previous studies of trace contaminants conducted on petroleum refinery wastewaters by PACE[1,2] and the American Petroleum Institute (API)[3].

In order to meet these objectives, a sampling program was carried out at two preselected refineries in Ontario. These refineries, and their effluent treatment facilities, were considered representative in terms of the range of process complexity and the design, age, configuration, and operation of the biological treatment system (see Appendix A for details of the selection). The sampling program, as defined by the Project Steering Committee,

involved the collection of 6-hour flow proportioned composite samples of influent to the biological treatment plant and effluent from the biological treatment plant, on six occasions over a two week period (i.e. every second day), at each refinery. During the sampling period, plant operational parameters and critical refinery operating conditions were documented. The data generated as a result of the sampling program were analyzed to address the stated objectives.

The analytical program focused on a comprehensive list of conventional contaminants, metals, volatile organic compounds and base neutral extractable compounds. Other classes of compounds were not included in the study based on the findings of both previous characterization studies (PACE[1,2], API[3]) and site specific effluent characterization work.* These studies indicated that the frequency of detection for compounds other than those analyzed was very low.

This report presents the findings of this study. Section 2.0 contains a brief description of the refineries and a description of the biological treatment plants that were sampled, a description of the sampling programs, and the analytical and statistical methodologies used in this study. Section 3.0 presents and discusses the results of the quality control program and the results of the monitoring program at each plant in terms of biological treatment plant operation, contaminant concentrations, and variability in the influent and effluent streams. Section 4.0 presents a discussion of the practicability of using a surrogate parameter for measuring trace contaminant removal performance, and a review of previous studies on refinery effluents. The conclusions and recommendations generated by the monitoring program are presented in Section 5.0. Appendices B thru I present a more detailed description of the sampling program, the analytical methods utilized, and the QA/QC program and results.

* Data reviewed by MOE July 1986 as part of the Municipal Industrial Strategy for Abatement program for the petroleum sector.

2.0 METHODOLOGY

2.1 Refinery and Biological Treatment Plant Descriptions

2.1.1 Esso Refinery, Sarnia

The Esso Petroleum Canada Refinery in Sarnia has the capacity to process 126,000 barrels of crude oil per day. Refinery facilities enable the processing of diverse crude stocks into over 340 different fuel products, petrochemical feedstocks, lubricating oils and waxes.

Water from a number of sources at the refinery is ultimately discharged to the St. Clair River. All oil-contacting waters (including process water, storm water and ship ballast water) are treated physically and biologically before discharge. Non-oil contacting water (once-through cooling water) is discharged directly to the river after physical treatment in API separators. A schematic of the liquid drainage and treatment system at Esso Refinery is presented in Figure 1.

Treatment of process water, ship ballast water and storm water initially takes place through gravity (API) separators, which reduce free oils and suspended solids. Dual media filters further reduce oil and fine suspended solids from the wastewater. Finally, wastewater is treated in the biological treatment facility, an activated sludge plant, before discharge into the St. Clair River.

Sour water (water high in ammonia, phenols or hydrogen sulphide) is pre-treated separately before joining the main oil-contacting stream. Ammonia and hydrogen sulphide are stripped from the wastewater in a sour water stripper, and stripped water is pretreated in a biological treatment unit (Aero Accelerators) to reduce phenols. This pretreated wastewater then joins the flows to the activated sludge plant.

Figure 2 presents a schematic of the activated sludge plant. The plant consists of two parallel completely mixed aeration tanks. Air is supplied by two mechanical aerators in each tank and diffused air at the ends of each tank. Phosphoric acid (as a nutrient supplement) is added continuously to the aeration tanks. Secondary clarification occurs in four rectangular clarifiers. Final effluent streams from the clarifiers combine prior to discharge to the river. Settled sludge from the clarifiers is returned to the aeration tanks by parallel screw pumps. Waste activated sludge is diverted from the recycle sludge system to two aerobic, batch-operated digesters.

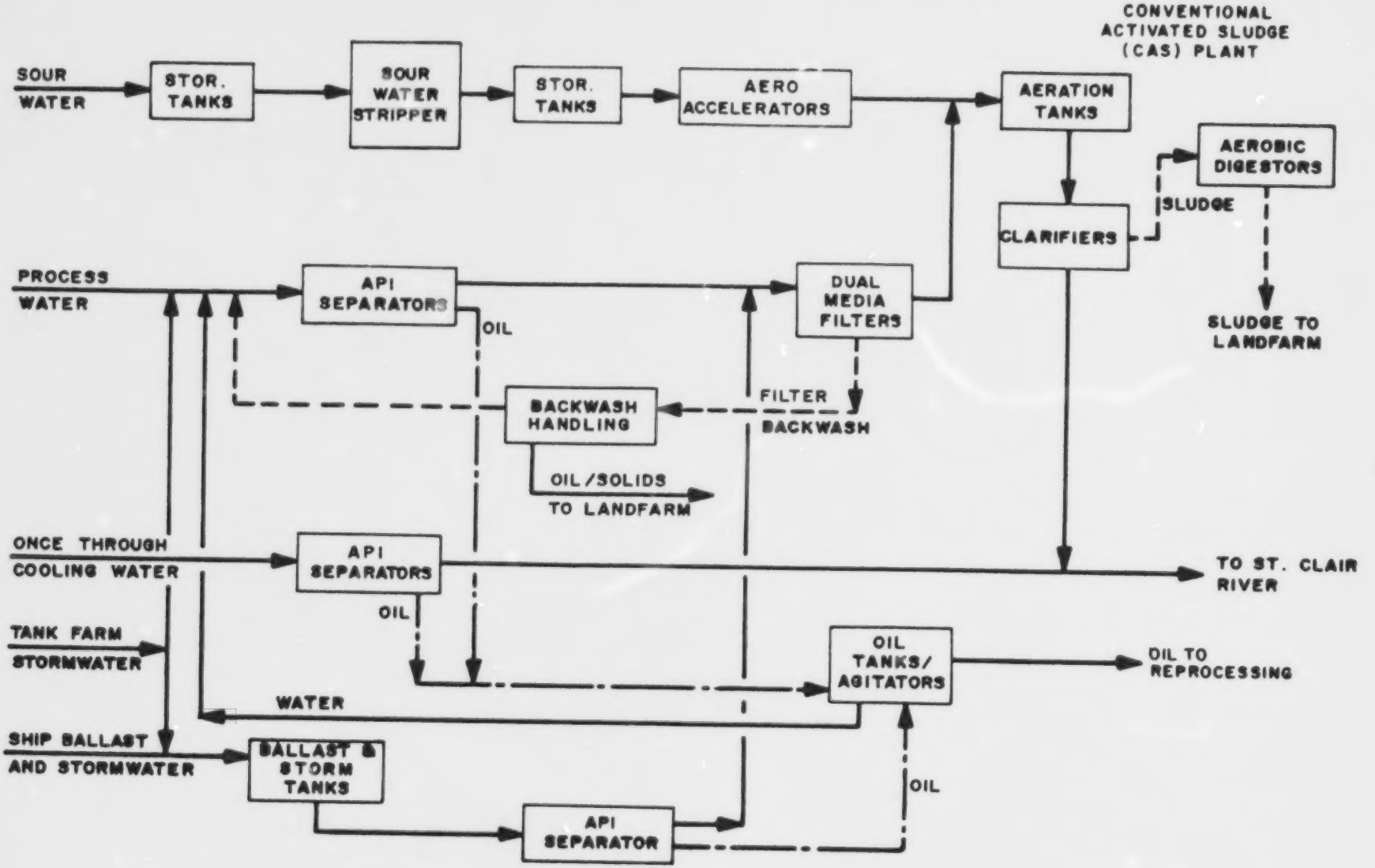

FIGURE 1 – SIMPLIFIED SCHEMATIC OF ESSO, SARNIA LIQUID EFFLUENT DRAINAGE & TREATMENT SYSTEM

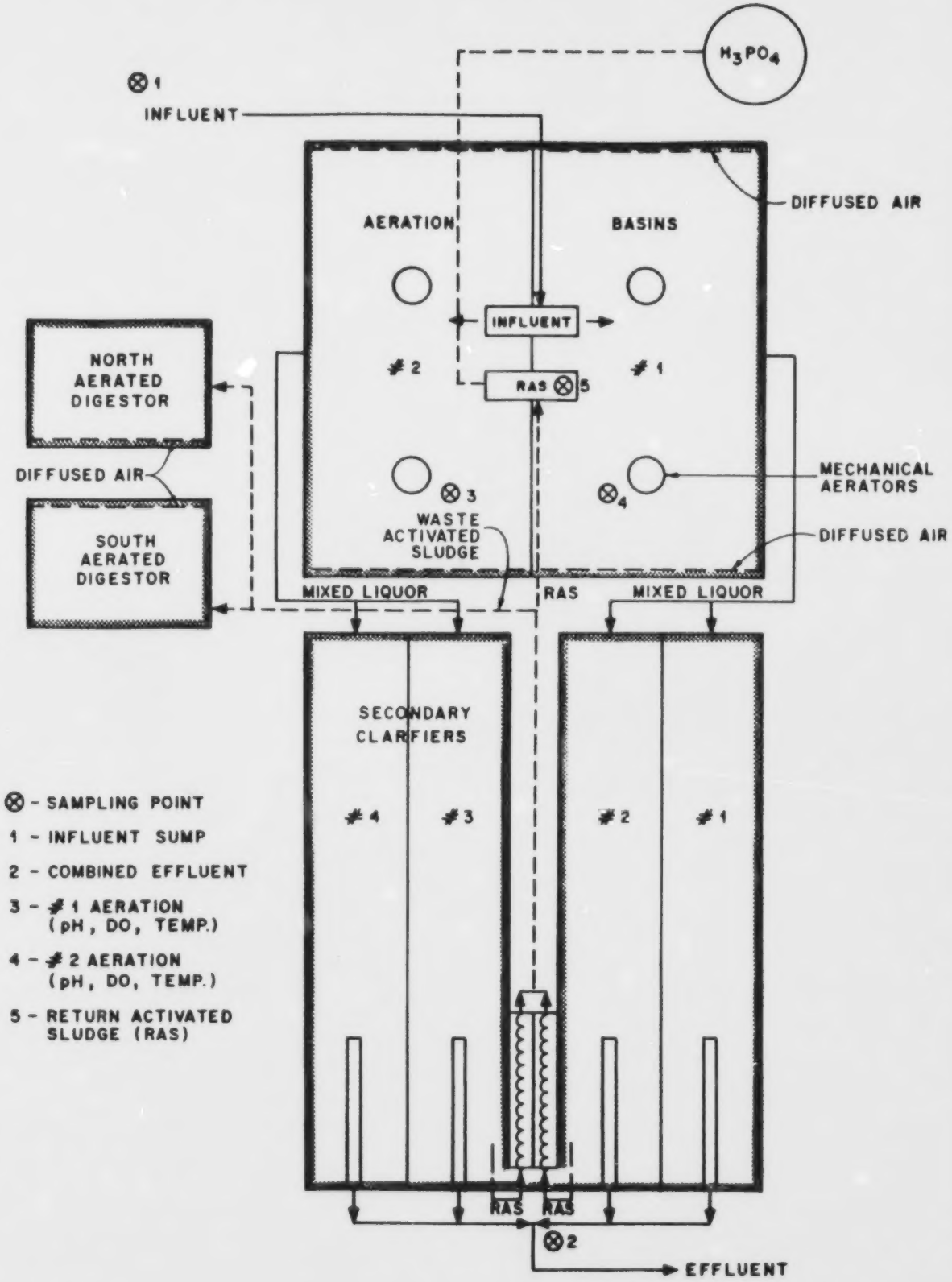

FIGURE 2 - SCHEMATIC OF ESSO REFINERY, SARNIA ACTIVATED SLUDGE PLANT

The activated sludge plant has an average design flow capacity of 22,700 m^3/day. The total aeration tank volume of 5,472 m^3 provides an aeration tank hydraulic retention time of 5.8 hours at average design flow. The total clarifier surface area of 1,784 m^2 results in a surface overflow rate of 12.7 $m^3/m^2 \cdot day$. Two aerated digesters operated in batch mode provide a total volume of 908 m^3 for digestion.

2.1.2 Petro-Canada Trafalgar Refinery

Petro-Canada Trafalgar Refinery has the capacity to process 85,000 barrels of crude oil per day. Major refinery processes at Petro-Canada Refinery include distillation, reforming, alkylation, desulphurization and blending of crude to produce a variety of petroleum products including gasolines, diesel and aviation fuels, liquid petroleum gases, heating and fuel oils, asphalt and sulphur.

A schematic of the liquid drainage and treatment system at the Petro-Canada Trafalgar Refinery is presented in Figure 3. Water from the refinery includes stormwater, process waters, ballast waters and cooling water blowdown. Uncontaminated stormwater and cooling water blowdown is collected in a surface drain system and discharged to natural drainages around the refinery. It passes through an oil trap lagoon to a surge lagoon for physical treatment before discharge. Oil-contacting stormwater is treated in an oil separator and usually discharged via a surge lagoon to Lake Ontario. If the stormwater is not suitable for discharge, it can be diverted to the effluent treater for further treatment. Process wastewater treatment involves oil/water separation in API separators, equalization, further oil and solids removal in induced air flotation (IAF) separators and biological treatment. Ballast water is collected in a ballast water storage tank, treated in an IAF separator for gross oil separation, then treated with process wastewaters in the effluent treater.

A schematic of the biological treatment system, an activated sludge plant, at the Petro-Canada Refinery is presented in Figure 4. The plant consists of three sets of aeration tanks in series: east and west primary aeration, north and south primary aeration and north and south secondary aeration. All tanks are covered and air is supplied by a diffused air system. There was no nutrient (phosphoric acid) addition to the aeration tanks at the time of sampling.

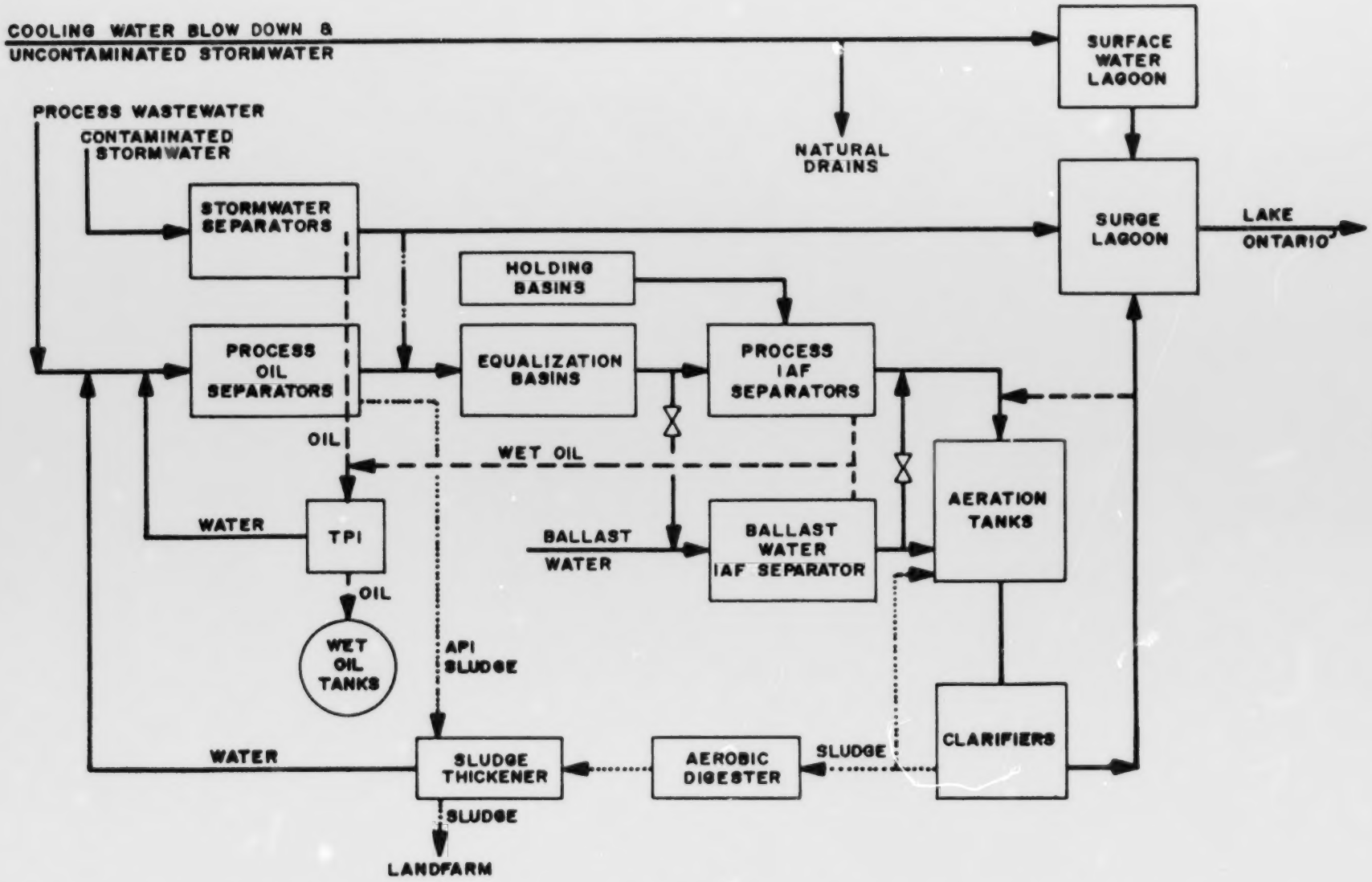

FIGURE 3 - SCHEMATIC OF TRAFALGAR REFINERY LIQUID EFFLUENT DRAINAGE & TREATMENT SYSTEM

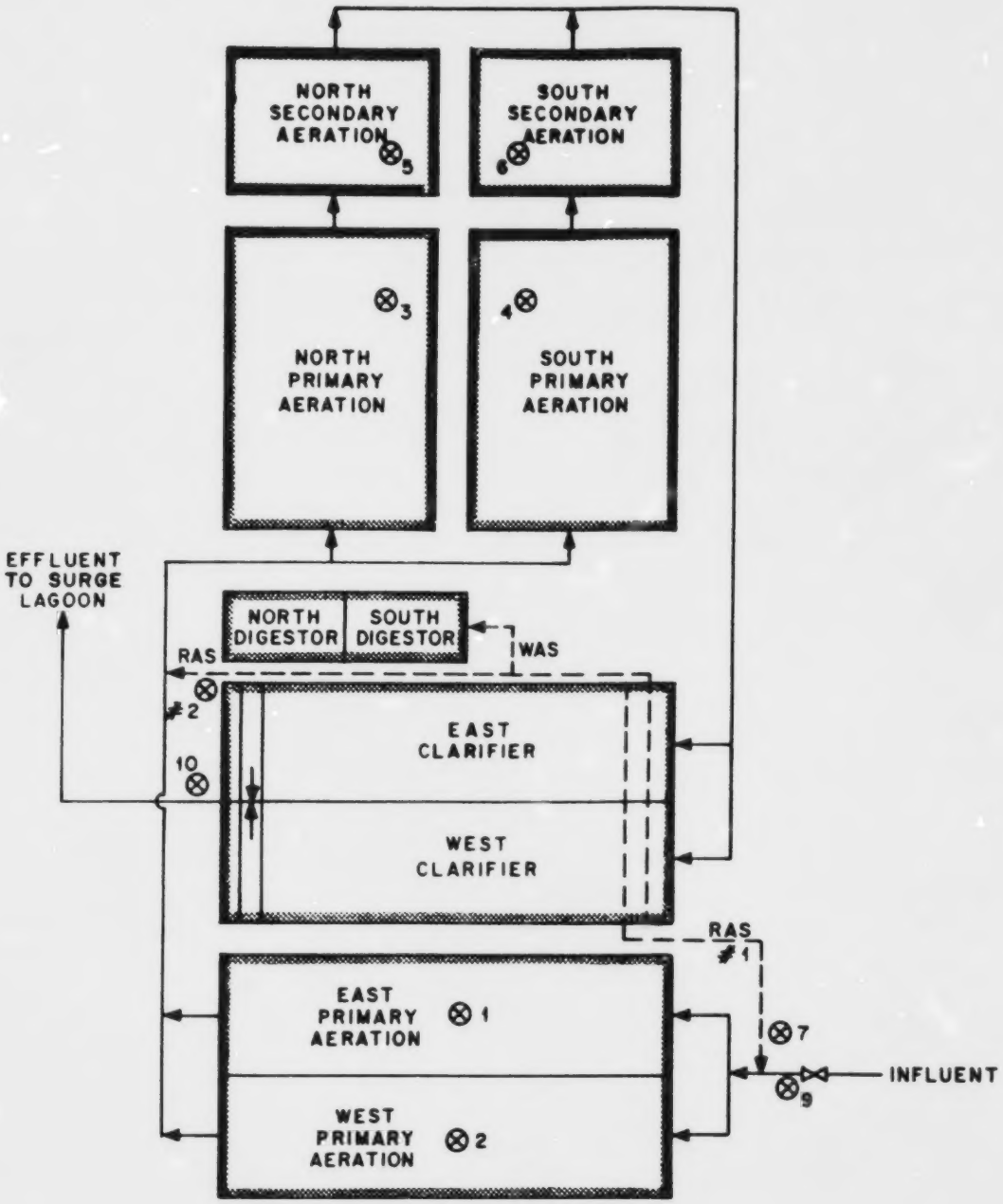

FIGURE 4 - SCHEMATIC OF PETRO CANADA, TRAFALGAR BIOLOGICAL WASTE WATER TREATMENT PLANT

As shown in the process schematic (Figure 4), sludge from the clarifiers is returned to two locations in the aeration system. The majority of the return sludge flow is transferred by air lift pumps to the inlet end of the east and west primary aeration tanks. A second return sludge flow is pumped to a splitter box where sludge is divided into a waste sludge flow to the aerobic digesters and a return sludge flow to the inlet of the north and south primary aeration tanks.

The activated sludge plant has an average design flow capacity of 6,019 m^3/day. The total aeration tank volume of 1,336 m^3 provides 5.3 hours of aeration tank hydraulic retention time at average design flow. The total clarifier surface area of 118 m^2 results in a surface overflow rate of 51.0 $m^3/m^2 \cdot d$.

2.2 Sampling Programs

The sampling programs at Esso Refinery, Sarnia and Petro Canada Trafalgar Refinery involved collection of a biological treatment plant influent sample and effluent sample on every second day of an eleven day sampling period, resulting in six samples of each stream. Effluent sampling was lagged to account for hydraulic retention time in the system; that is, a time equivalent to the average hydraulic retention time in the system was provided between the time that influent and effluent samples were collected. All samples were manually composited 6-hour flow proportioned samples. Sampling occurred during the eleven day periods beginning 15 September 1986 at Esso Refinery, and 16 September 1986 at Petro-Canada Refinery.

At the Esso Refinery activated sludge plant, collection of twelve effluent samples took place during an additional sampling period (11-22 August 1986). Two effluent samples were collected every second day of the eleven day period. A 12 hour time interval was left between the start of each sample collection.

On each sampling day of the three sampling periods, grab samples of mixed liquor were monitored for oxygen uptake rates and sludge settleability. Both mixed liquor and return (waste) sludge grab samples were collected on these days and analyzed for total suspended solids and volatile suspended solids. Field measurement of dissolved oxygen concentrations, temperature and pH in each cell of the aeration tanks were taken at each site once each sampling day. At each site, waste activated sludge volumes were recorded for

the monitoring period to enable the calculation of the solids retention time (SRT) for that period. Reference should be made to Figures 2 and 4 for the sampling and aeration tank monitoring locations at the Esso Refinery and the Petro-Canada Refinery treatment systems, respectively.

During the August sampling period at the Esso Refinery, a concurrent study on behalf of Esso Chemical in Sarnia involved sampling of the service water used at the Esso Chemical Plant and the Esso Refinery. Six 6-hour composite samples of St. Clair River water were collected on every second day of the 11 day period beginning 12 August 1986. Samples were collected and handled similar to the Esso Refinery activated sludge plant samples and preserved and stored at the same location in the refinery.

Appendix B describes the sample handling methodologies used in terms of sample collection, preservation and storage.

2.3 Analytical Methods

Table 1 specifies the contaminants measured in influent and effluent samples at the Esso Refinery and Petro-Canada Refinery activated sludge plants during the September sampling periods. Also indicated are those parameters measured in the Esso Refinery effluent and service water during the August sampling periods.

The analysis of conventional contaminants, and total and volatile suspended solids in the mixed liquor and return sludge, were conducted at CANVIRO's Kitchener laboratory. Trace contaminants (metals, base neutral extractable organics, and volatile organic compounds) were analyzed by CAN TEST Ltd. in Vancouver, B.C.

Appendix C presents the analytical methods used for analysis of conventional contaminants, total metals and trace organic compounds.

2.4 QA/QC Program

For the purposes of maintaining the accuracy and precision of field and laboratory analysis to ensure scientific credibility, a thorough QA/AC program was carried out. The investigation was under strict quality assurance procedures from the initial step of sample bottle preparation through

TABLE 1: LIST OF COMPOUNDS MEASURED IN INFLUENT AND EFFLUENT SAMPLES

Volatile Organic compounds, including:

- Benzene*
- Bromodichloromethane
- Bromoform
- Bromomethane
- Carbon Tetrachloride
- Chlorobenzene
- Chloroethane
- 2-Chloroethylvinyl ether
- Chloroform
- Chloromethane
- bis-Chloromethyl ether
- Dibromochloromethane
- Dichlorodifluoromethane
- 1,1-Dichloroethane
- 1,2-Dichloroethane
- 1,1-Dichloroethylene
- trans-1,2-Dichloroethylene
- 1,2-Dichloropropane
- cis-1,3-Dichloropropane
- trans-1,3-Dichloropropane
- Ethylbenzene*
- Methylene Chloride
- 1,1,2,2-Tetrachloroethane
- 1,1,2,2-Tetrachloroethene
- Toluene*
- 1,1,1-Trichloroethane
- 1,1,2-Trichloroethane
- Trichloroethylene
- Trichlorofluoromethane
- Vinyl Chloride
- Xylenes*

Base-Neutral Extractable Organics, including:

Various PAH's*, including

- Acenaphthene
- Acenaphthylene
- Anthracene
- Benzo(a)anthracene
- Benzo(b)fluoranthene
- Benzo(k)fluoranthene
- Benzo(a)pyrene
- Chrysene
- Fluoranthene
- Fluorene
- Indeno(1,1,2-c,d)pyrene
- Naphthalene
- Phenanthrene
- Pyrene

Various Chlorinated Benzenes

Various Phthalate Esters

Various Haloethers

Total Metals:*

- Arsenic (As)
- Cadmium (Cd)
- Chromium (Cr)
- Copper (Cu)
- Iron (Fe)
- Lead (Pb)
- Mercury (Hg)
- Nickel (Ni)
- Zinc (Zn)

Conventional Parameters:*

- Dissolved Organic Carbon (DOC)
- Oil and Grease
- Total phenolics
- Suspended solids (TSS)
- pH
- Alkalinity
- Ammonia (NH_3-N)
- Nitrate (NO_3-N)
- Nitrite (NO_2-N)
- Conductivity
- Kjeldahl nitrogen (TKN)
- Phosphorus

* Parameters measured in Esso Refinery effluent (11-22 August) and service water (12-23 August).

sample collection, sample transport, analysis and subsequent report generation. Appendix D presents a detailed description of the QA/QC program utilized in the field and in analysis at CANVIRO and CAN TEST for all of the sampling periods.

As an additional check, effluent activated sludge plant samples were collected on one day during one sampling period at each refinery and analyzed at the MOE laboratory in Rexdale, Ontario. Samples were collected, composited and preserved in prepared and labelled containers supplied by MOE. These were then shipped directly to the laboratory the following day for analysis.

2.5 MOE Toxicity Tests

Biological treatment plant effluent samples were collected on one day at both Petro-Canada Refinery and Esso Refinery for the purpose of conducting toxicity tests. Twenty-two litre samples were collected each hour during the regular 6-hour effluent sampling routine, resulting in a total sample volume of approximately 135 litres. This sample was received by the MOE Laboratory the day after it was collected.

The toxicity tests conducted at the MOE laboratory were 96-hour static fish bioassays using juvenile rainbow trout.

2.6 Statistical Methods

In order to determine efficient estimates of mean and variance for the influent and effluent data sets for each parameter, it was necessary to identify an appropriate frequency distribution which was representative of the analytical data. When plotted on log normal probability paper, some parameters showed a definite log normal distribution. Plots of selected parameter distributions are presented in Appendix E. The other parameters (typically conventional contaminants) had so little variance that sample means and variances for log normal and normal distributions were similar. For consistency, sample means and variances and confidence intervals for all of the parameters were based on a log normal distribution.

In many cases, trace contaminant concentrations in both influent and effluents were below the detection limit. For the purposes of calculating sample means and confidence intervals, it was necessary to assume values

for those contaminants that were not detected above the minimum compound detection limit. Concentrations of compounds that were non-detectable were arbitrarily set at one half of the detection limit. If, however, a particular contaminant was detected in less than half of the samples, the above procedure was not applied because it would have resulted in a double peaked distribution. Therefore, in these cases mean and 95 percent confidence range calculations were not conducted.

It should be noted that the small number of samples (6) in most cases did not allow verification of the assumed population distribution. Further, in arbitrarily assuming that non-detectable compounds were present at a concentration equal to one half of the detection limit, a bias may have been introduced.

In order to further characterize the sampled streams, the frequency of detection (FOD) of a particular contaminant was also calculated. This number represented the percentage of the total samples taken of a stream in which the contaminant was detected above the minimum detection limit.

3.0 RESULTS OF MONITORING PROGRAM

3.1 QA/QC Results

A detailed presentation of the QA/QC program results is provided in Appendix F. With respect to conventional contaminants (except oil and grease), total metals, and volatile and base neutral extractable organic compounds, good reproducibility was generally found in laboratory and field methods for CANVIRO, CAN TEST and MOE results.

Oil and grease at low levels (4 to 9.5 mg/L) was reported for all field blanks and a laboratory blank. The sensitivity of the oil and grease test at low levels (i.e. <5 mg/L) and the consistent positive indication of contamination in the field blanks suggested that the oil and grease values reported by CANVIRO in the sample streams may be higher than actual concentrations.

Phthalate esters [bis-(2-ethylhexyl) phthalate, di-n-butylphthalate, di-n-octylphalate, diethylphthalate] found regularly in samples were also consistently detected in field blank samples and were probably a result of contamination. These compounds are commonly associated with plastic materials, and were likely present as a result of the various plastic materials used in the field (i.e. plastic distilled water container, plastic gloves, etc.).

3.2 Esso Refinery, Sarnia

3.2.1 Refinery Operation During Sampling Periods

Parameters describing the refinery operating conditions, including crude type and throughput, treatment of storm water and ballast water in the biological treatment plant, and rainfall, refinery upsets and shutdowns that would affect process wastewater quality were recorded throughout the influent and effluent sampling period (15-26 September 1986). Most of these parameters were also recorded for the additional effluent sampling period (11-22 August 1986). A detailed record of these parameters is presented in Appendix G.

During the September monitoring period, the refinery processed an average of 105,000 barrels per day of crude oil (83 percent of the refinery capacity). Except for the exceptionally heavy rainfall during this period,

refinery operation was considered typical by Esso staff. The rainfall caused activated sludge plant flows to reach a maximum of 127% of design dry weather capacity on 15 September. However, only 52 percent of the wet weather peak flow capacity (56,400 m^3/day) was reached.

3.2.2 Activated Sludge Plant Operation During Sampling Periods

During both monitoring periods (11-22 August and 15-26 September 1986) at the Esso Refinery in Sarnia, a number of biological treatment plant operating parameters were recorded. Table 2 presents the operating conditions that existed at the Esso Refinery activated sludge plant during these sampling periods.

Although flows were variable in the second period as a result of the heavy rainfalls experienced, the average flow of 23,440 m^3/d was comparable to the average flow for the first period of 23,195 m^3/d. The resulting average aeration tank hydraulic retention time was 5.6 hours for both periods.

During the first sampling period, sludge wasting resulted in a solids retention time of 63.0 days and an average mixed liquor concentration of 5,980 mg/L. A much larger volume of sludge was wasted during the second period, which reduced the solids retention time to 35.8 days and the average mixed liquor concentration to 5,450 mg/L.

In the aeration tanks, the average dissolved oxygen concentration was 2.3 mg/L, the average temperature was 32°C and pH values were neutral. Good sludge settleability was indicated by an average sludge volume index (SVI) of 89. The average specific oxygen uptake rate in the aeration tanks was found to be 0.051 g O_2/g VSS·d. With the exception of the variable flows, steady plant operating conditions were maintained throughout both sampling periods.

3.2.3 Analytical Data

3.2.3.1 Conventional Contaminants and Metals

The conventional contaminants and metals found in influent and effluent streams during the two sampling periods are presented in Table 3.

TABLE 2: ESSO REFINERY - ACTIVATED SLUDGE PLANT OPERATING PARAMETERS

		AERATION NO. 1								AERATION NO. 2								WASTE ACTIVATED SLUDGE		
DATE	FLOW ($10^3 m^3/d$)	MLSS (mg/L)	VSS (%)	DO (mg/L)	T (°C)	pH	SPECIFIC O_2 UPTAKE RATE (g O_2/g VSS.d)	30 MINUTE SETTLING VOLUME (mL)	SVI	MLSS (mg/L)	VSS (%)	DO (mg/L)	T (°C)	pH	SPECIFIC O_2 UPTAKE RATE (g O_2/g VSS.d)	30 MINUTE SETTLING VOLUME (mL)	SVI	TSS (mg/L)	VOLUME (m^3)	EST. SRT (days)
11/8	24.18	5080	76.0	4.3	32	7.2	0.026	352	69	6160	77.9	3.7	32	7.0	0.030	460	75	12,300	10.2	
13/8	24.36	5260	78.3	3.9	32	7.2	0.020	500	95	6600	77.9	3.3	32	7.3	0.040	600	91	13,880	51.5	
15/8	23.31	5400	77.8	2.1	36	6.9	0.038	400	74	7280	78.3	1.7	36	6.9	0.038	750	103	12,920	51.5	
17/8	21.20	5400	76.3	1.1	34	7.0	0.061	350	65	6500	77.2	0.6	34	7.0	0.063	460	71	13,880	14.5	63.0
19/8	23.81	5580	74.2	1.2	35	7.0	0.038	390	70	6740	76.6	0.7	35	6.9	0.045	520	77	12,720	18.7	
21/8	22.31	5220	79.3	1.2	36	6.8	0.051	380	73	6560	77.1	1.1	36	6.9	0.046	500	76	13,720	18.7	
15/9	29.18	4840	75.2	4.8	27	6.3	0.026	340	70	5740	75.6	4.3	27	6.7	0.026	780	135	12,160	54.4	
17/9	19.65	4960	75.0	2.9	29	6.7	0.038	380	77	6340	72.2	1.7	29	6.7	0.032	850	134	11,700	108.9	
19/9	20.45	5400	75.0	3.4	31	6.8	0.051	430	80	6550	75.6	3.1	31	6.8	0.053	910	139	12,600	108.9	
21/9	18.32	5350	75.7	3.3	31	6.7	0.047	430	80	6700	74.6	2.4	31	6.7	0.053	920	137	11,500	272.1	35.8
23/9	26.50	4600	73.9	1.2	30	6.9	0.138	380	83	5250	75.2	0.4	30	6.9	0.122	500	95	12,450	246.6	
25/9	26.54	4500	75.6	1.4	29	6.6	0.059	370	84	5200	76.0	0.8	29	6.6	0.086	430	83	6,800	28.9	

TABLE 3: CONCENTRATION OF CONVENTIONAL CONTAMINANTS AND METALS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT ESSO REFINERY, SARNIA

		SAMPLE PERIOD 1												SAMPLE PERIOD 2						
	DATE	11 AUG		13 AUG		15 AUG		17 AUG		19 AUG		21 AUG		15 SEP	17 SEP	19 SEP	21 SEP	23 SEP	25 SEP	
	DAY	1-AM	1-PM	2-AM	2-PM	3-AM	3-PM	4-AM	4-PM	5-AM	5-PM	6-PM	6-PM	1	2	3	4	5	6	
Conventional Parameters																				
pH	Influent													7.4	7.0	7.2	7.2	8.3	7.4	
	Effluent	7.1	7.3	7.1	7.2	7.2	7.1	7.1	6.9	7.2	6.9	7.4	7.2	6.7	6.8	7.2	7.1	6.9	6.8	
Conductivity (umhos/cm)	Influent													760	780	1140	790	600	900	
	Effluent	890	570	450	570	570	570	850	900	820	910	710	570	590	710	670	640	600	730	
Alkalinity (mg/L as $CaCO_3$)	Influent													75.7	99.8	127.2	107.3	122.5	122.1	
	Effluent	14	72	69	60	53	44	54	74	55	57	64	51	58	65	61	59	95	53	
Suspended Solids (mg/L)	Influent													70	40	24	16	60	26	
	Effluent	NA	13	NA	11	NA	3	NA	8	NA	6	NA	7	30	7	6	4	8	6	
Dissolved Organic Carbon (mg/L)	Influent													15.7	17.4	25.4	26.6	55.0	24.3	
	Effluent	11.5	10.6	11.5	11.9	11.7	11.8	12.5	12.8	12.8	12.2	9.4	8.8	8.8	10.4	11.6	10.8	15.0	11.9	
Total Kjeldahl Nitrogen (mg/L)	Influent													6.3	7.7	12.1	11.5	27.4	10.2	
	Effluent	NA	3.04	NA	2.38	NA	2.58	NA	2.74	NA	2.01	NA	3.74	2.4	1.6	NA	3.6	13.0	2.3	
Ammonia-Nitrogen (mg/L)	Influent													<1	<1	<1	<1	<1	<1	
	Effluent	NA	<1.0	NA	<1.0	NA	<1.0	NA	<1.0	NA	<1.0	NA	<1.0	<0.01*	1*	<0.01*	<0.01*	10.9*	<1	
Nitrate Nitrogen (mg/L)	Influent													0.54	0.28	0.49	0.54	0.20	0.15	
	Effluent	4.7	3.5	4.0	5.8	7.4	6.8	6.4	3.6	8.3	6.8	5.8	6.2	0.20	0.54	6.9	5.8	0.20	6.2	
Nitrite Nitrogen (mg/L)	Influent													0.041	<0.01	0.01	0.01	0.023	<0.01	
	Effluent	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.011	<0.01	<0.01	0.01	<0.01	<0.01	<0.01	<0.01	0.027	
Total Phenols (ug/L)	Influent													129.7	104.9	165.5	300	277.3	326.2	
	Effluent	5.4	8.0	10.4	9.4	10.6	8.0	8.0	12.6	11.2	12.0	13.1	15.4	4.0	7.4	6.6	5.4	3.4	6.0	
Phosphorus (Total) (mg/L) (Filtered)	Influent													<0.3	0.51	0.64	0.79	0.31	0.78	
	Effluent	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.32	0.18	0.45	0.65	0.13	0.54	
Oil and Grease (mg/L)	Influent													18.4†	12.1†	9.3†	6.5†	14.9†	10.4†	
	Effluent	NA	7†	NA	6†	NA	7†	NA	7†	NA	7†	NA	6†	8†	5†	5†	9†	6†	6†	DET. LIMIT
Metals																				
Arsenic (ug/L)	Influent													4	4	3	5	4	5	
	Effluent	6	3	5	5	5	6	4	5	4	5	5	3	7	5	5	4	8	3	1
Cadmium (ug/L)	Influent													ND	ND	ND	ND	ND	ND	
	Effluent	3	ND	ND	1	ND	ND	2	ND	2	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
Chromium (ug/L)	Influent													5	2	2	2	5	4	
	Effluent	22	2	3	2	43	2	6	3	1	1	3	1	2	2	2	1	2	1	1
Copper (ug/L)	Influent													23	13	7	8	17	10	
	Effluent	7	9	8	9	10	5	5	9	10	180	10	12	13	6	2	6	3	1	1
Iron (ug/L)	Influent													2230	770	730	690	1560	850	
	Effluent	270	310	110	190	330	170	90	165	190	150	180	150	520	99	94	77	310	99	30
Lead (ug/L	Influent													13	5	3	2	10	7	
	Effluent	10	5	4	5	30	2	2	2	1	5	2	2	19	3	2	1	2	2	1
Mercury (ug/L)	Influent													0.05	ND	0.12	0.08	0.07	ND	
	Effluent	.08	.06	.06	.05	.06	.06	.06	.05	ND	ND	ND	.05	0.05	0.13	0.20	0.08	0.05	0.05	0.05
Nickel (ug/L)	Influent													9	3	2	1	6	8	
	Effluent	8	3	8	4	46	4	5	6	8	10	10	10	3	5	1	1	6	5	1
Zinc (ug/L)	Influent													120	36	36	22	74	44	
	Effluent	39	38	28	37	32	26	30	26	66	57	50	34	38	27	23	16	ND	110	10

NA = Not Analyzed
ND = Not Detected
* = Analyzed using specific ion electrode method (Refer to Appendix C).
† = Oil and grease concentrations reported may be higher than actual values (Refer to Appendix F).

In terms of conventional parameters, influent and effluent pH values were in the neutral range (6.7-8.3). A 76 percent removal efficiency of influent TSS concentrations of 34 mg/L (geometric mean) resulted in a mean effluent concentration of 8 mg/L. The average removal efficiency for DOC was 55 percent, with mean influent and effluent concentrations of 25.0 and 11.3 mg/L, respectively.

Influent TKN concentrations were less than 12.1 mg/L, except for one high value of 27.4 mg/L on 23 September. Removal of TKN took place to achieve an effluent concentration of less than 3.7 mg/L on all days measured except 23 September, where the effluent concentration was 13.0 mg/L. Although ammonia analyses were repeated in the Kitchener laboratory three times for each influent sample, influent ammonia concentrations were less than the detection level (1 mg/L) in all samples. Ammonia was detected only once in the effluent stream, at a concentration of 10.9 mg/L on 23 September. The significant difference between ammonia and TKN values suggests that nitrogen was present in the influent as an organic nitrogen compound. In all influent samples, nitrate-nitrogen concentrations were found to be less than 0.54 mg/L. Effluent nitrate-nitrogen concentrations on all but three days were greater than 3.5 mg/L, indicating nitrate production through the activated sludge plant. The high SRTs maintained during the monitoring periods, the removal of TKN and the production of nitrate-nitrogen all provide evidence that the plant was nitrifying.

Phenol concentrations in the influent were relatively low (mean 188 ug/L) as a result of the pretreatment of high phenolic wastewaters in the Aero Accelerators upstream of the activated sludge plant. An average phenol removal efficiency of 96 percent was achieved, resulting in a mean effluent phenol concentration of 7.7 ug/L.

Oil and grease concentrations in the influent were also low (mean 11 mg/L) as a result of the thorough pretreatment of wastewater at Esso Refinery. The mean concentrations of 11 mg/L and 6 mg/L for influent and effluent respectively resulted in an average removal efficiency of 43 percent. It is noted that the actual values may be lower than those reported as a result of laboratory error (refer to Appendix F).

Total metal concentrations, with the exception of Fe, were not found at levels greater than 120 ug/L in any influent or effluent samples.

Cd was not detected in any influent or effluent samples. The mean influent concentrations of As, Cr, Pb and Ni were between 3 and 5 ug/L. Mean influent concentrations of 12 ug/L for Cu, 47 ug/L for Zn and 0.053 ug/L for Hg were found. Average removal of metals through the activated sludge plant (excluding iron) for the September monitoring period were 67 percent for Cu, 49 percent for Zn, 40 percent for Pb, 33 percent for Cr, 25 percent for Ni and negligible for As and Hg.

3.2.3.2 Trace Organic Contaminants

The results of the analysis for trace organics in the influent and effluent are presented in Table 4.

Typically, volatile aromatic hydrocarbons (benzene, ethylbenzene, toluene and xylenes) were the only volatile organic compounds found in both influent and effluent streams. With the exception of 23 September, the maximum concentration of these compounds that was identified in any influent samples was 795 ug/L for xylenes. On 23 September, concentrations of all of the above compounds increased significantly. A benzene concentration of 1388 ug/L was measured during this sampling time. This increase coincided with the unusually high TKN and effluent ammonia concentrations also found on this day; however, there was no major upset reported at the refinery. Although there was an increase in influent volatile compound concentrations, effluent concentrations did not exceed 4.1 ug/L (except on one occasion for xylenes at 19.5 ug/L), and were often non-detectable. It should be noted that benzene, ethylbenzene and xylenes were also detected in one field blank sample at levels less than 4 ug/L. Benzene and xylenes were detectable (above 1 ug/L) in 50 and 44 percent respectively of the effluent samples. Ethylbenzene and toluene were detected in less than 12 percent of the effluent samples; methylene chloride was detected twice in effluent samples. Because this compound was not found in influent samples, it is likely that its presence was a result of contamination.

In addition to the target volatile compounds, a list of additional compounds detected during the analysis was developed by CAN TEST, and is presented in Appendix H. Of the 23 compounds qualitatively detected in at least one influent sample, none were detected in any effluent samples, indicating that excellent removal occurred in the biological system.

TABLE 4: CONCENTRATION OF TRACE ORGANICS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT ESSO REFINERY, SARNIA

	DATE	11 AUG		13 AUG		15 AUG		17 AUG		19 AUG		21 AUG		15 SEP	17 SEP	19 SEP	21 SEP	23 SEP	25 SEP	DET. LIMIT
	DAY	1-AM	1-PM	2-AM	2-PM	3-AM	3-PM	4-AM	4-PM	5-AM	5-PM	6-AM	6-PM	1	2	3	4	5	6	
Volatile Organic Compounds (ug/L)																				
Benzene	Influent													21	ND	80	336	1388	314	
	Effluent	1.2	ND	2.2	1.2	1.4	2.5	ND	1.8	1.5	2.3	ND	ND	ND	ND	ND	ND	1.2	ND	1.0
Toluene	Influent													3.6	ND	18	78	844	192	
	Effluent	ND	ND	ND	1.1	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9	ND	1.0
Ethylbenzene	Influent													ND	ND	ND	3.0	686	21	
	Effluent	ND	ND	ND	3.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.0
Xylenes	Influent													309	220	387	795	948	500	
	Effluent	ND	1.4	1.2	19.5	1.0	ND	ND	1.1	ND	1.4	ND	ND	2.6	ND	ND	ND	4.1	ND	1.0
Methylene Chloride	Influent													ND	ND	ND	ND	ND	ND	
	Effluent													ND	39*	ND	ND	ND	13*	1.0
Base Neutral Extractable Organics (ug/L)																				
Acenapthene	Influent													ND	ND	3.7	7.8	ND	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Methyl Anthracene	Influent													70	26	9.4	15	58	4.5	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
bis-(2-ethylhexyl) phthalate	Influent													19*	6.7*	3.0*	9.6*	66*	90*	
	Effluent	ND	7.8*	31.6*	2.4*	9.4*	7.3*	78*	60*	30*	3.2*	9.7*	3.8*	5.0*	35*	ND	61*	30*	14*	2.5
di-n-butylphthalate	Influent													ND	ND	ND	ND	4.4*	ND	
	Effluent	ND	ND	4.5*	ND	3*	ND	ND	3.8	ND	ND	10.1*	2.5*	ND	ND	ND	ND	ND	ND	2.5
di-n-octyl phthalate	Influent													ND	ND	ND	ND	ND	ND	
	Effluent	ND	ND	ND	3.7*	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Diethylphthalate	Influent													ND	ND	ND	ND	ND	ND	
	Effluent	ND	ND	4.9*	3.8*	2.5*	ND	4.5*	3.1*	ND	ND	4.8	3.3	ND	ND	ND	ND	ND	ND	2.5
Fluoranthene	Effluent													6.9	ND	2.3	ND	12.8	4.5	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.2
Fluorene	Influent													ND	ND	ND	ND	11.2	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Phenanthrene	Influent													ND	ND	ND	ND	8.9	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.4
Pyrene	Influent													16	4.0	3.3	4.3	ND	3.4	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Methyl Naphthalene	Influent													ND	ND	ND	ND	15	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Dimethyl Naphthalene	Influent													220	94	58	115	282	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Trimethyl Naphthalene	Influent													390	153	98	162	258	ND	
	Effluent	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0

ND = Not Detected

* = Suspected Contamination

COMPOUNDS NOT DETECTED

VOLATILE ORGANIC COMPOUNDS	BASE NEUTRAL EXTRACTABLE ORGANIC COMPOUNDS
Bromodichloromethane	Acenaphthylene
Bromoform	Anthracene
Bromomethane	bis (2-chloroethyoxyl) methane
Carbon Tetrachloride	bis (2-chloroethyl) ether
Chlorobenzene	bis (2-chloroisopropyl) ether
Chloroethane	Benzidine
2-Chloroethylvinyl ether	Benzo(a)anthracene
Chloroform	Benzo(a)pyrene
Chloromethane	Benzo(b)fluoranthene
bis-Chloromethyl ether	Benzo(g,h,i)perylene
Dibromochloromethane	Benzo(k)fluoranthene
1,1-Dichloroethane	Chrysene
1,2-Dichlorethane	Dibenzo(a,h)anthracene
1,1-Dichloroethylene	Hexachlorobenzene
trans-1,2-Dichloroethyl	Hexachlorobutadiene
1,2-Dichloropropene	Hexachlorethane
cis-1,3-Dichloropropene	Indeno(1,2,-c,d)pyrene
trans-1,3-Dichloropropene	Isophorone
1,1,2,2-Tetrachloroethene	N-nitrosodiphenylamine
1,1,2,2-Tetrachloroethane	Naphthalene
1,1,1-Trichloroethane	Nitrobenzene
1,1,2-Trichloroethane	1,2,4-Trichlorobenzene
Trichloroethylene	1,2-Dichlorobenzene
Trichlorofluoromethane	1,3-Dichlorobenzene
Vinyl Chloride	1,4-Dichlorobenzene
	2,4-Dinitrotoluene
	2,6-Dinitrotoluene
	2-chloronephthalene
	3,3'-Dichlorobenzidine
	4-Bromophenyl phenyl ether
	4-chlorophenyl phenyl ether

NOTES:

1) Influent samples were not collected in August sampling period.

2) Methylene chloride was not analyzed for in August sampling period.

A number of polynuclear aromatic hydrocarbons (PAHs) were found in the influent stream (acenaphthene, methyl anthracene, fluoranthene, pyrene, methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene). Trimethyl naphthalene was present at the highest concentration of all of the PAH compounds found, at a maximum of 390 ug/L. PAHs were not found in any effluent samples above minimum compound detection limits, indicating that excellent removal was occurring in the biological process.

The only other base neutral extractable organic compounds detected were various phthalate esters [bis-(2-ethylhexyl) phthalate, di-n-butylphthalate, di-n-octylphthalate and diethylphthalate] which were found in both influents and effluents. As these compounds are common plastizers and were found in field blanks, it is likely their presence was a result of contamination.

3.2.4 Statistical Analysis of Results

Statistical analyses were carried out on the analytical data in order to determine concentration variability, represented by the 95 percent confidence interval. Also included in the statistical analysis is the frequency of detection (FOD); that is, the number of samples, represented as a percentage of the total, in which a specific contaminant was present at a concentration above the detection limit.

It should be noted that statistical analysis done on the entire population (i.e. 18 samples) may have been biased towards the first sampling period. Two samples were taken per day during the first period, resulting in 12 samples from this period and only 6 from the second period.

Table 5 presents the geometric mean, maximum and minimum concentrations of measured parameters in the influent and effluent streams. Variability of the parameter, represented by the 95 percent confidence interval, and frequency of detection (FOD, percent) are also presented.

In terms of conventional contaminants, it can be seen that the 95 percent confidence ranges for pH, alkalinity, TSS, DOC, phenols and oil and grease are small relative to the ranges for influents. The effect of biological and hydraulic dampening in the process produced low effluent variability for these parameters.

TABLE 5: STATISTICAL ANALYSIS OF CONTAMINANT CONCENTRATIONS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT ESSO REFINERY, SARNIA

	SIX INFLUENT 6-HOUR COMPOSITE SAMPLES					SIX EFFLUENT 6-HOUR COMPOSITE SAMPLES[a]					EIGHTEEN EFFLUENT 6-HOUR COMPOSITE SAMPLES[b]					DET. LIMIT
PARAMETERS	FOD	MEAN	MIN	MAX	95% CONFIDENCE RANGE	FOD	MEAN	MIN	MAX	95% CONFIDENCE RANGE	FOD	MEAN	MIN	MAX	95% CONFIDENCE RANGE	
Conventional																
pH	100	7.4	7.0	8.3	6.9 - 7.9	100	6.9	6.7	7.2	6.7 - 7.1	100	7.1	6.7	7.4	7.0 - 7.2	
Conductivity (umhos/cm)	100	813	600	1140	637 - 1037	100	654	590	730	592 - 724	100	671	450	910	608 - 741	
Alkalinity (mg/L as $CaCO_3$)	100	108	76	127	86 - 134	100	64	53	95	51 - 81	100	56	14	95	46 - 68	
Suspended Solids (mg/L)	100	34	16	70	18 - 67	100	8	4	30	4 - 18	100	8	3	30	5 - 11	
Dissolved Organic Carbon (mg/L)	100	25.0	15.7	55.0	15.1 - 41.6	100	11.3	8.8	15.0	9.2 - 13.8	100	11.3	8.8	15.0	10.6 - 12.1	
Ammonia Nitrogen (mg/L)	0	*	ND	ND	*	33	*	ND	10.9	*	17	*	ND	10.9	*	1.0
Total Kjeldhal Nitrogen (mg/L)	100	11.1	6.3	27.4	6.2 - 19.9	100	3.3	1.6	13.0	1.3 - 8.3	100	3.2	1.6	13.0	1.8 - 12.6	
Nitrate Nitrogen (mg/L)	100	0.33	0.15	0.54	0.2 - 0.6	100	1.3	0.20	6.9	0.2 - 9.8	100	2.8	0.2	8.3	1.4 - 5.6	
Nitrite Nitrogen (mg/L)	67	0.02	ND	0.041	0.01 - 0.03	33	*	ND	0.027	*	22	*	ND	0.027	*	0.01
Total Phenols (ug/L)	100	188	105	326	115 - 308	100	5.2	4.0	7.4	3.7 - 7.5	100	7.7	4.0	15.4	6.0 - 9.8	
Total Phosphorus (mg/L)	100	0.46	<0.30	0.79	0.30 - 0.97	-	-	-	-	-	-	-	-	-	-	
Filtered Phosphorus (mg/L)	-	-	-	-	-	100	0.33	0.13	0.65	0.16 - 0.68	100	0.33	0.13	0.65	0.16 - 0.68	
Oil and Grease (mg/L)†	100	11	7	18	7 - 17	-	6	5	9	5 - 8	100	6	5	9	6 - 7	
Metals (mg/L)																
Arsenic	100	4	3	5	3 - 5	100	5	3	8	3 - 8	100	5	3	8	6 - 10	1
Cadmium	0	*	ND	ND	*	0	*	ND	ND	*	4	*	ND	3	*	1
Chromium	100	3	1	5	2 - 5	100	2	1	2	1 - 2	100	3	1	43	2 - 5	1
Copper	100	12	7	23	7 - 20	100	4	1	13	1 - 11	100	8	1	180	5 - 15	1
Iron	100	1023	690	2230	587 - 1784	100	150	77	520	61 - 370	100	161	77	520	122 - 213	30
Lead	100	5	2	13	2 - 12	100	3	1	19	1 - 9	100	3	1	30	2 - 5	1
Mercury	67	0.053	ND	0.120	ND - 0.110	100	0.080	0.050	0.20	0.041-0.157	83	0.056	ND	0.20	0.043 - 0.073	0.05
Nickel	100	4	1	9	1 - 10	100	3	1	6	1 - 7	100	5	1	46	4 - 8	1
Zinc	100	47	22	120	24 - 94	83	33	ND	110	15 - 76	94	32	ND	110	24 - 44	10
Volatile Organic Compounds (ug/L)																
Benzene	83	73	ND	1388	2.7 - 1988	17	*	ND	1.2	*	50	ND	ND	2.5	ND - 1.2	1.0
Ethylbenzene	50	4	ND	686	ND - 119	0	*	ND	ND	*	6	*	ND	3.4	*	1.0
Toluene	83	27	ND	844	1.2 - 616	17	*	ND	1.9	*	11	*	ND	1.9	*	1.0
Xylenes (O,P,M)	100	467	220	948	245 - 887	33	*	ND	4.1	*	44	*	ND	19.5	ND - 1.6	1.0
Methylene Chloride**	0	*	ND	ND	*	33	*	ND	39	*	33	*	ND	39	*	2.8
Base Neutral Extractable Organic Compounds																
Methyl Anthracene	100	20	4.5	70	5.9 - 68	0	*	ND	ND	*	0	*	ND	ND	*	2.0
Acenaphthene	17	*	ND	7.8	*	0	*	ND	ND	*	0	*	ND	ND	*	1.9
bis (2-ethylhexyl)phthalate**	100	17	3	90	3.6 - 77	83	21.4	ND	61	7.2 - 63.7	89	11	ND	78.0	5.7 - 21.3	2.5
Di-n-butyl phthalate**	17	*	ND	4.4	*	0	*	ND	ND	*	28	*	ND	10.1	*	2.5
Di-n-octyl phthalate**	0	*	ND	ND	*	0	*	ND	ND	*	6	*	ND	3.7	*	2.5
Di-ethylphthalate**	0	*	ND	ND	*	0	*	ND	ND	*	39	*	ND	4.9	*	2.5
Fluorene	17	*	ND	11.2	*	0	*	ND	ND	*	0	*	ND	ND	*	1.9
Fluoranthene	67	3	ND	12.8	ND - 10.2	0	*	ND	ND	*	0	*	ND	ND	*	2.2
Methyl Naphthalene	17	*	ND	15	*	0	*	ND	ND	*	0	*	ND	ND	*	2.0
Dimethyl Naphthalene	83	58	ND	282	5.4 - 631	0	*	ND	ND	*	0	*	ND	ND	*	2.0
Trimethyl Naphthalene	83	79	ND	390	6.4 - 984	0	*	ND	ND	*	0	*	ND	ND	*	2.0
Phenanthrene	17	*	ND	8.9	*	0	*	ND	ND	*	0	*	ND	ND	*	5.4
Pyrene	83	4	ND	16	1.3 - 10.9	0	*	ND	ND	*	0	*	ND	ND	*	1.9

ND = Not Detected.

FOD = Frequency of detection (percent) above minimum detection limit.

MEAN = Logarithmic mean.

* = Summary statistics not calculated for those parameters that were detected on fewer than one half of samples.

** = Possible Contamination.

† = Oil and grease concentrations reported may be higher than actual values (Refer to Appendix F).

Note: Values reported as ND were counted as detects for the statistical analysis and included in the calculations of mean and 95% confidence range as one half of the detection limit.

[a]Six effluent samples were collected in September at the same time as influent sample data presented.

[b]Twelve of eighteen effluent samples were collected during August and comparative influent samples are not available for this time period.

With respect to trace organics (excluding phthalate esters), the volatile aromatic compounds (benzene, ethylbenzene, toluene and xylenes), methyl anthracene, fluoranthene, pyrene, dimethylnaphthalene and trimethyl naphthalene were detected in at least 50 percent of the influent samples. In effluents, benzene and xylenes were not detected in greater than 50 percent of the samples, ethylbenzene and toluene were detected in less than 12 percent of the samples, and there were no base neutral extractable compounds (with the exception of phthalates) detected in any samples.

Ninety-five percent confidence intervals for trace organic compounds (excluding phthalate esters and methylene chloride) indicate that there was some variability in influent concentrations and virtually none in effluent concentrations (since they were generally below the detection limit).

3.2.5 Comparison of Service Water to Final Effluent

A concurrent study carried out by CANVIRO involved sampling of the Esso Refinery service water from the St. Clair River. Six 6-hour composite samples of the service water were taken every second day of an eleven day sampling period beginning 12 August 1986. Table 6 presents a summary of the statistical comparison of the characteristics of the service water and the activated sludge plant effluent.

With respect to conventional contaminants, logarithmic mean concentrations of suspended solids, dissolved organic carbon, total kjeldahl nitrogen, nitrate nitrogen, total phenols and oil and grease were only slightly higher for the activated sludge plant effluent than the service water. All of the mean metal concentrations were slightly higher for the activated plant effluent than the service water.

Benzene and xylenes were detected more frequently in the service water and at higher (log) mean concentrations than in the activated sludge plant effluent. Ethylbenzene was found in both streams at similar frequencies and concentrations. Toluene, detected only 11 percent of the time in the activated sludge plant effluent samples, was non-detectable in the service water samples.

Of the base neutral extractable compounds measured, only phthalate esters were detected in both streams. These were more frequently found, and at higher concentrations, in the activated sludge plant effluent than in the service water.

TABLE 6: COMPARISON OF FREQUENCY OF DETECTION, MEAN, MAXIMUM AND MINIMUM CONTAMINANT CONCENTRATIONS BETWEEN SERVICE WATER AND ACTIVATED SLUDGE PLANT EFFLUENT AT ESSO REFINERY

	SIX SERVICE WATER 6-HOUR COMPOSITES				EIGHTEEN ACTIVATED SLUDGE PLANT EFF. 6-HOUR COMPOSITES				DET. LIMIT
PARAMETERS	FOD	MEAN	MIN	MAX	FOD	MEAN	MIN	MAX	
Conventional									
pH	100	7.7	7.2	8.0	100	7.1	6.7	7.4	
Conductivity (umhos/cm)	100	151	80	190	100	671	450	910	
Alkalinity (mg/L as $CaCO_3$)	100	76	71	80.5	100	55.8	13.6	95.0	
Suspended Solids (mg/L)	100	5	2	12	100	8	3	30	
Dissolved Organic Carbon (mg/L)	100	4.6	3.8	5.2	100	11.3	8.8	15.0	
Ammonia Nitrogen (mg/L)	0	*	ND	ND	17	ND	ND	10.9	1.0
Total Kjeldahl Nitrogen (mg/L)	17	ND	ND	1	100	3.2	1.6	13.0	1.0
Nitrate Nitrogen (mg/L)	100	0.45	0.36	0.74	100	2.8	0.2	8.3	
Nitrite Nitrogen (mg/L)	0	*	ND	ND	22	*	ND	0.027	0.01
Total Phosphorus (mg/L)	0	*	ND	ND	-	-	-	-	
Filtered Phosphorus (mg/L)	-	-	-	-	100	0.33	0.13	0.65	0.13
Total Phenols (ug/L)	67	1.6	ND	3.4	100	7.7	4.0	15.4	
Oil and Grease (mg/L)†	100	5	3	8	100	6	5	9	
Metals (ug/L)									
Arsenic	0	*	ND	ND	100	5	3	8	1
Cadmium	17	*	ND	1	22	*	ND	2	1
Chromium	100	2	1	26	100	3	1	43	1
Copper	100	7	4	13	100	8	1	180	1
Iron	83	106	ND	240	100	161	77	520	30
Lead	67	1	ND	2	100	3	1	30	1
Mercury	0	*	ND	ND	83	0.056	ND	0.20	0.05
Nickel	100	3	2	11	100	5	1	46	1
Zinc	100	18	11	29	94	32	ND	110	10
Volatile Organics (ug/L)									
Benzene	100	1.8	1.2	2.9	50	ND	ND	2.5	1.0
Ethylbenzene	17	*	ND	3.4	6	*	ND	3.4	1.0
Toluene	0	*	ND	ND	11	*	ND	1.9	1.0
Xylenes	67	2.2	ND	32	44	ND	ND	19.5	1.0
Base Neutral Extractable Organics (ug/L)									
bis (2-ethylhexyl)phthalate**	0	*	ND	ND	100	11	ND	78.0	2.5
Di-n-butyl phthalate**	17	*	ND	2.9	28	*	ND	10.1	2.5
Di-n-octyl phthalate**	0	*	ND	ND	6	*	ND	3.7	2.5
Di-ethylphthalate**	0	*	ND	ND	39	*	ND	4.9	2.5

ND = Not Detected.

FOD = Frequency of detection (percent) above minimum detection limit.

MEAN = Logarithmic mean.

* = Summary statistics not calculated for those parameters that were detected in fewer than one half of samples.

** = Possible contamination.

† = Oil and grease concentrations reported may be higher than actual values (Refer to Appendix F).

3.2.6 MOE Toxicity Test Results

Static bioassay toxicity tests were done using juvenile rainbow trout on final effluent collected 21 August 1986 from the Esso Refinery, Sarnia activated sludge plant. Test results indicated that this effluent was non-lethal to trout at 100 percent concentration over the 96 hour test period. Results are presented in detail in Appendix I.

3.3 Petro-Canada Trafalgar Refinery

3.3.1 Refinery Operation During Sampling Period

During the sampling period (16-27 September) at Petro-Canada Trafalgar Refinery, a number of parameters describing refinery operating conditions were recorded. These included crude throughput rate and type, rainfall, input of ballast water to the biological treatment plant and refinery upsets and shut downs which might effect process wastewater quality to the biological treatment plant. Appendix G contains a summary table of the information recorded for the sampling period.

The refinery was processing an average of 57,000 barrels of crude oil per day, 67 percent of refinery capacity, during the monitoring period. Although rainfall was heavy, runoff normally collected in the storm water drain system was not diverted to the biological treatment plant during the period. Storm water normally entering the process sewers was processed in the biological plant during rainfall events. Ballast water flows were treated for the first two sampling days. The refinery has an on-going problem with the IAF separators that treat process wastewaters before biological treatment. This results in poor oil separation and typically high influent oil and grease concentrations to the activated sludge plant. There were no other upsets reported and, with the exception of a 4 hour amine plant shut down on 16 September, refinery operation was considered typical by refinery staff.

3.3.2 Biological Treatment Plant Operation During Sampling Period

The plant operating conditions for the sample period are presented in Table 7.

TABLE 7: PETRO-CANADA TRAFALGAR REFINERY - ACTIVATED SLUDGE PLANT OPERATING PARAMETERS

		PRIMARY AERATION NO. 1									PRIMARY AERATION NO. 2									SECONDARY AERATION									WAS		
DATE	FLOW ($10^3 m^3/d$)		MLSS (mg/L)	VSS (%)	DO (mg/L)	T (°C)	pH	SPECIFIC O_2 UPTAKE RATE (g O_2/g VSS.d)	30 MINUTE SETTLING VOLUME (mL)	SVI		MLSS (mg/L)	VSS (%)	DO (mg/L)	T (°C)	pH	SPECIFIC O_2 UPTAKE RATE (g O_2/g VSS.d)	30 MINUTE SETTLING VOLUME (mL)	SVI		MLSS (mg/L)	VSS (%)	DO (mg/L)	T (°C)	pH	SPECIFIC O_2 UPTAKE RATE (g O_2/g VSS.d)	30 MINUTE SETTLING VOLUME (mL)	SVI	TSS (mg/L)	VOLUME (m^3)	EST. SRT (days)
16/9	6.088	EPA	1500	80.6	1.2	34	8.0				NPA	1550	77.4	0.2	34	7.4	0.724	300	193	NSA	1600	75.0	0.1	34	7.7	0.751	320	200			
		WPA	1550	76.7	2.5	34	8.1	0.924	260	168	SPA	1140	66.7	0.5	34	7.4				SSA	1500	73.3	0.1	34	7.7				3100	0	
18/9	6.091	EPA	1500	65.6	2.8	32	7.5	0.711	300	200	NPA	1480	70.3	0.5	32	7.2				NSA	1340	62.3	0.1	32	7.1						
		WPA	1220	73.3	3.0	32	7.5				SPA	1540	77.9	0.8	32	7.2	0.474	530	344	SSA	1520	72.4	0.2	32	7.1	0.535	420	276	2500	0	
20/9	4.594	EPA	1800	77.8	1.6	36	7.5				NPA	1550	83.9	0.1	35	7.2	0.608	300	194	NSA	1350	96.3	0.3	35	7.2	0.562	330	244			
		WPA	1750	77.1	2.6	36	7.5	0.851	260	149	SPA	1350	96.3	0.1	35	7.2				SSA	1400	96.4	0.2	35	7.2				2550	16.7	5.7
22/9	4.133	EPA	1400	96.4	3.0	37	7.7	0.549	300	214	NPA	1450	93.1	1.0	37	7.3				NSA	2050	92.7	0.4	37	7.3						
		WPA	1500	96.7	3.0	37	7.9				SPA	1650	97.0	1.5	37	7.3	0.266	360	218	SSA	2000	80.0	0.1	37	7.3	0.261	350	175	2700	0	
24/9	4.925	EPA	1550	77.4	1.5	39	7.7				NPA	1850	78.4	0.1	39	7.4	0.640	270	146	NSA	1850	78.4	0.1	39	7.3	0.659	270	146	2150		
		WPA	1650	81.8	3.0	39	7.8	1.123	250	151	SPA	1950	79.5	1.3	39	7.4				SSA	2050	75.6	0.2	39	7.3					0	
26/9	3.974	EPA	1500	76.7	1.9	39	7.6	0.911	340	226	NPA	1450	82.9	0.2	39	7.3				NSA	1650	84.8	0.2	39	7.3						
		WPA	1400	89.3	3.0	39	7.6				SPA	1750	88.6	0.1	39	7.3	0.585	370	211	SSA	1650	87.9	0.5	39	7.3	0.611	360	218	2200	0	

EPA = East primary aeration
WPA = West primary aeration

SPA = South primary aeration
NPA = North primary aeration

SSA = South secondary aeration
NSA = North secondary aeration

Flows during the eleven day sampling period ranged from 3,974 to 6,088 m^3/day or 60 to 100 percent of the design flow. The average dissolved oxygen concentrations were 2.4 mg/L for the east and west primary aeration tanks, 0.4 mg/L for the north and south primary aeration tanks and 0.2 mg/L for the north and south secondary aeration tanks. The average temperature found in the aeration tanks was 36°C; pH values were neutral (7.3-8.0).

Despite the fact that there was virtually no sludge wasted intentionally, a high level of solids carryover the clarifier weirs, due to poor sludge settleability and high clarifier hydraulic loadings, occurred throughout the period, resulting in a low solids retention time (SRT) of 5.7 days.

The average mixed liquor concentration in the aeration tanks was 1500 mg/L. Poor sludge settleability was shown by the average sludge volume index (SVI) of 200. The average oxygen uptake rate was 0.59 g O_2/g VSS·d.

At Petro-Canada Refinery, SRTs were low (5.7 days compared to greater than 35.8 days at Esso Refinery), dissolved oxygen concentration were low (0.2-2.4 mg/L compared to 2.3 mg/L) and temperatures were high (36°C compared to 32°C). Mixed liquor solids concentration were lower at Petro-Canada Refinery than at Esso Refinery (1500 mg/L compared to greater than 5400 mg/L), the sludge settleability was poorer (SVI of 200 compared to SVI of 89) and there was a high specific oxygen utilization rate (0.59 g O_2/g VSS·d compared to 0.051 g O_2/g VSS·d). Also, at the Petro-Canada Refinery activated sludge plant, there was no nutrient phosphorus supplement as there was at the Esso activated sludge plant.

3.3.3 Analytical Data

3.3.3.1 Conventional Contaminants and Metals

Table 8 presents the conventional contaminants and metal concentrations found in influent and effluent samples from the Petro Canada refinery biological treatment (activated sludge) plant.

Although pH values showed the influent to be slightly basic (9.2-9.9), these were neutralized in the aeration basins, resulting in effluents in the neutral pH range (7.2 to 7.7). The suspended solids were present in the effluent, as a result of sludge carry over the clarifier weirs, at a mean (geometric) concentration of 64 mg/L. An average of 60 percent removal of the mean influent DOC concentration of 45.0 mg/L produced a mean effluent concentration of 17.8 mg/L.

TABLE 8: CONCENTRATIONS OF CONVENTIONAL CONTAMINANTS AND METALS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT PETRO-CANADA TRAFALGAR

		DATE	16 SEP	18 SEP	20 SEP	22 SEP	24 SEP	26 SEP	
		DAY	1	2	3	4	5	6	
pH	Influent		9.8	9.2	9.6	9.9	9.69	9.4	
	Effluent		7.1	7.2	7.3	7.7	7.4	7.5	
Conductivity (umhos/cm)	Influent		--	1100	1270	1300	1525	1400	
	Effluent		--	1200	1340	--	1580	1500	
Alkalinity (mg/L as $CaCO_3$)	Influent		161	163	144	128	142	157	
	Effluent		147	141	141	79	170	166	
Suspended Solids (mg/L)	Influent		55	50	60	60	50	70	
	Effluent		70	80	50	70	60	60	
Dissolved Organic Carbon (mg/L)	Influent		49.3	40.3	51.6	41.5	44.6	43.5	
	Effluent		18.9	16.0	19.3	16.9	16.3	20.1	
Total Kjeldahl Nitrogen (mg/L)	Influent		17.4	21.6	14.8	26.4	27.4	23.0	
	Effluent		15.4	19.4	12.4	25.0	26.4	22.3	
Ammonia-Nitrogen (mg/L)	Influent		15.4	19.3	13.1	24.6	25.0	20.6	
	Effluent		11.6	14.8	9.7	18.6	20.3	15.8	
Nitrate Nitrogen (mg/L)	Influent		0.63	0.58	2.2	1.9	0.50	1.5	
	Effluent		0.23	0.26	0.43	0.57	0.15	0.7	
Nitrite Nitrogen (mg/L)	Influent		0.12	0.25	0.15	0.13	0.21	0.19	
	Effluent		<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	
Total Phenols (ug/L)	Influent		17200	18650	22700	27500	28500	23000	
	Effluent		84.3	40.4	62.8	42.0	36.7	52.2	
Phosphorus (Total) (mg/L) (Filtered)	Influent		1.08	0.93	1.37	0.36	1.47	1.23	
	Effluent		<0.15	0.15	<0.15	<0.15	0.68	0.68	
Oil and Grease (mg/L)	Influent		19†	12†	17†	18†	30†	47†	
	Effluent		21†	29†	15†	18†	27†	23†	
Metals									DET. LIMIT
Arsenic (ug/L)	Influent		38	24	64	57	31	58	
	Effluent		37	27	61	61	43	44	1
Cadmium (ug/L)	Influent		ND	ND	ND	ND	ND	ND	
	Effluent		ND	ND	ND	ND	ND	ND	1
Chromium (ug/L)	Influent		320	180	300	250	300	300	
	Effluent		260	31	250	310	310	250	1
Copper (ug/L)	Influent		9	6	7	1	6	11	
	Effluent		8	12	11	16	1	6	1
Iron (ug/L)	Influent		1420	880	1070	700	1050	1290	
	Effluent		1390	1550	1370	1280	1280	990	30
Lead (ug/L	Influent		20	13	13	11	14	16	
	Effluent		16	19	12	20	18	14	1
Mercury (ug/L)	Influent		0.20	0.25	0.43	0.29	0.27	0.25	
	Effluent		0.28	0.20	0.12	0.33	0.40	0.33	0.05
Nickel (ug/L)	Influent		25	3	7	3	6	5	
	Effluent		3	16	6	1	5	5	1
Zinc (ug/L)	Influent		150	92	120	85	115	130	
	Effluent		130	170	140	150	130	140	10

† Oil and grease concentrations reported may be higher than actual values (Refer to Appendix F).

There was only 8 percent removal of influent TKN (mean 21.3 mg/l) and 23 percent removal of influent ammonia (mean 19.2 mg/L), resulting in mean effluent concentrations of 19.5 and 14.7 mg/L respectively. There was about 33 percent nitrate removal from mean influent concentrations of 1.02 mg/L and there was no nitrite detected in effluent samples. Since there was no significant ammonia removal, no nitrate production, a relatively short SRT (5.7 days) and limited dissolved oxygen in the aeration tanks, it was concluded that the plant was not nitrifying.

Because there was no pretreatment of high phenolic wastewaters at the Petro-Canada Refinery as there was at the Esso Refinery, influent phenols at the Petro-Canada Refinery of 22,544 ug/L (mean) were significantly higher than those found at Esso Refinery (mean 188 ug/L). Phenol removal efficiencies of greater than 99.5 percent were achieved within the biological system, although effluent concentrations remained high (mean 50.8 ug/L) compared to the Esso Refinery (mean 7.7 ug/L).

Influent total phosphorus concentrations varied from 0.36 to 1.47 mg/L. Effluent soluble phosphorus concentrations were often non-detectable, indicating that there was phosphorus deficiency in the biological process.

Influent oil and grease concentrations (mean 21.5 mg/L) were not removed within the biological treatment plant resulting in high effluent oil and grease concentrations (mean 21.4 mg/L). It should again be noted that the actual oil and grease concentrations may be lower than those reported (Refer to Appendix D).

The influent metal concentrations to the biological treatment plant were higher at Petro-Canada Refinery for As, Cr, Fe, Pb, Hg, and Zn, than at Esso Refinery. Mean influent concentrations of metals were found to be 43 ug/L for As, 270 ug/L for Cr, 5 ug/L for Cu, 1040 ug/L for Fe, 14 ug/L for Pb, 0.28 ug/L for Hg, 6 ug/L for Ni and 113 ug/L for Zn. Since there was no metal removal through the treatment plant, effluent concentrations were similar.

3.3.3.2 Trace Organics

The results from the analyses of trace organics are presented in Table 9.

TABLE 9: CONCENTRATIONS OF TRACE ORGANICS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT PETRO-CANADA, TRAFALGAR

	DATE	16 SEP	18 SEP	20 SEP	22 SEP	24 SEP	26 SEP	DET. LIMIT
	DAY	1	2	3	4	5	6	
Volatile Organic Compounds (ug/L)								
Benzene	Influent	1450	3070	1969	1430	1194	891	
	Effluent	ND	ND	ND	ND	ND	ND	1.0
Toluene	Influent	1240	1850	1099	925	927	698	
	Effluent	ND	ND	ND	ND	ND	ND	1.0
Ethylbenzene	Influent	142	177	145	123	90	81	
	Effluent	ND	ND	ND	ND	ND	ND	1.0
Xylenes	Influent	953	807	614	587	589	625	
	Effluent	ND	ND	ND	ND	ND	ND	1.0
Chloroform	Influent	ND	1.8*	ND	ND	ND	ND	
	Effluent	ND	ND	ND	1.8*	ND	ND	1.6
1,2-Dichloropropane	Influent	179	ND	59	20	19	9	
	Effluent	41	30	9.5	ND	ND	ND	6.0
Methylene Chloride	Influent	ND	ND	ND	ND	ND	ND	
	Effluent	ND	13*	ND	5.8*	ND	ND	2.8
Base Neutral Extractable Organics (ug/L)								
Anthracene	Influent	227	ND	ND	ND	ND	ND	
	Effluent	ND	ND	ND	ND	ND	ND	3.5
Methyl Anthracene	Influent	503	240	235	290	303	366	
	Effluent	ND	ND	ND	ND	ND	ND	2.0
bis (2-ethylhexyl) phthalate	Influent	30.8*	ND	9.9*	90.6*	32.3*	10.8*	
	Effluent	19.4*	ND	27.1*	120 *	29.4*	33.6*	2.5
di-n-butylphthalate	Influent	ND	ND	ND	ND	ND	ND	
	Effluent	ND	ND	4.7*	ND	ND	4.9*	2.5
Fluorene	Influent	96	75	81	75	104	149	
	Effluent	ND	ND	ND	ND	ND	ND	2.2
Naphthalene	Influent	278	189	280	239	226	232	
	Effluent	ND	ND	ND	ND	ND	ND	1.6
Phenanthrene	Influent	54	131	135	184	149	164	
	Effluent	ND	ND	ND	ND	ND	ND	5.4
Methyl Naphthalene	Influent	2710	2410	2120	2490	2490	2600	
	Effluent	ND	ND	ND	ND	ND	ND	2.0
Dimethyl Naphthalene	Influent	3570	2050	2540	2010	3680	3434	
	Effluent	3	ND	12.8	ND	ND	ND	2.0
Trimethyl Naphthalene	Influent	2160	2090	1550	2090	2200	2600	
	Effluent	7.6	ND	44	ND	ND	ND	2.0

VOLATILE COMPOUNDS NOT DETECTED	BASE NEUTRAL COMPOUNDS NOT DETECTED
Bromodichloromethane	Acenaphthene
Bromoform	Acenaphthylene
Bromomethane	bis-(2-chloroethyxyl) methane
Carbon Tetrachloride	bis-(2-chloroethyl) ether
Chlorobenzene	bis-(2-chloroisopropyl) ether
Chloroethane	Benzidine
2-Chloroethylvinyl ether	Benzo(a)anthracene
Chloroform	Benzo(a)pyrene
Chloromethane	Benzo(b)fluoranthene
Dibromochloromethane	Benzo(g,h,i)perylene
Dichlorodifluoromethane	Benzo(k)fluoranthene
1,1-dichloroethane	Chrysene
1,2-dichloroethane	Di-n-octylphthalate
1,1-dichloroethylene	Dibenzo(a,h)anthracene
Trans-1,2-Dichloroethylene	Diethylphthalate
Cis-1,3-Dichloropropene	Dimethylphthalate
Trans-1,3-dichloropropene	Hexachlorobenzene
1,2-Dichloropropylene	Hexachlorobutadiene
1,1,2,2-Tetrachloroethane	Hexachlorethane
1,1,2,2-Tetrachloroethene	Indeno(1,2,-c,d)pyrene
1,1,1-Trichloroethane	Isophorone
1,1,2-Trichloroethane	Nitrobenzene
Trichloroethylene	Pyrene
Trichlorofluoromethane	1,2,4-Trichlorobenzene
Vinyl Chloride	1,2-Dichlorobenzene
	1,3-Dichlorobenzene
	1,4-Dichlorobenzene
	2,4-Dinitrotoluene
	2,6-Dinitrotoluene
	2-chloronaphthalene
	3,3'-Dichlorobenzidine
	4-Bromophenyl phenyl ether
	4-Chlorophenyl phenyl ether

ND = Not Detected

* Possible contamination

Volatile aromatic hydrocarbons were found in all influent samples at mean concentrations of 1,540 ug/L for benzene, 1,071 ug/L for toluene, 584 ug/L for xylenes and 122 ug/L for ethylbenzene. These concentrations were significantly higher than those measured for Esso Refinery influent samples. None of these compounds were detectable in any of the Petro-Canada biological treatment plant effluent samples. One additional volatile organic compound, 1,2-dichloropropane, was detected at a mean concentration of 21.8 ug/L in the influent. Although removal occurred, a mean effluent concentration of 8.3 ug/L was found for effluent samples. Chloroform was detected at low levels (1.8 ug/L) in one influent and one effluent sample. Methylene chloride was detected twice at low levels (<12 ug/L) in effluent samples. Since it was not detected in any influent sample, its presence was probably a result of contamination.

A list was developed by CAN TEST of additional volatile organic compounds that were qualitatively identified during sample analysis, and is presented in Appendix H. Of the 14 compounds detected at least once in an influent sample, only 2 compounds were detected once in an effluent sample, indicating excellent removal of volatile compounds in the biological process.

A number of polynuclear aromatic hydrocarbons (PAHs) (anthracene, methyl anthracene, fluorene, naphthalene, phenanthrene, methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene) were consistently found in the influent samples. Methyl anthracene, fluorene, phenanthrene, methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene were common to Esso Refinery influent samples although they were detected more frequently and/or at higher concentrations in Petro-Canada samples. Methyl naphthalene, dimethyl naphthalene and trimethyl naphthalene had the highest influent concentrations of 2,463, 2,948 and 2,091 ug/L (means), respectively, in Petro-Canada Refinery samples. Although most PAH compounds were not detected in the effluent streams, dimethyl and trimethyl naphthalene were detected on two separate occasions at concentrations of up to 44 ug/L.

Phthalate esters [bis-(2-ethylhexyl) phthalate and di-n-butyl-phthalate] detected in the samples, were also detected in the field blanks. Since these compounds are commonly associated with plastic, it is probable that their existence in the sample is a result of contamination from plastic materials or equipment used in the field or laboratory.

3.3.4 *Statistical Analysis*

Table 10 presents the mean (logarithmic), maximum and minimum concentrations of the measured parameters in influent and effluent streams. Variability of the parameter, represented by the 95 percent confidence range, and mean frequency of detection (FOD) are also presented.

In terms of conventional contaminants, the variability in influent samples became dampened in the biological treatment process to produce less variable effluent concentrations for all conventional parameters except suspended solids, TKN, NH_3 and oil and grease. There was little or no removal of these contaminants across the biological treatment process.

Mean influent and effluent total metal concentrations and variability were similar since there was no metal removal in the activated sludge plant.

With respect to volatile organic compounds, all of the volatile aromatic hydrocarbons (benzene, ethylbenzene, toluene and xylenes) were detected in 100 percent of the influent samples. 1,2-dichloropropane was detected in 83 percent of the influent samples and in 50 percent of the effluent samples.

With the exception of anthracene, all of the PAH compounds (anthracene, methyl anthracene, fluorene, naphthalene, phenanthrene, methyl naphthalene, dimethylnaphthalene and trimethyl naphthalene) found in influent samples were present in 100 percent of the samples.

Dimethyl naphthalene and trimethyl naphthalene, each at a 33 percent frequency of detection, were the only PAH compounds detected in effluent samples.

3.3.5 MOE Toxicity Test Results

Static bioassay toxicity tests were conducted on Petro Canada Refinery biological treatment plant effluent collected 16 September 1986. The results reported from MOE indicated that after 96 hours there was 0 percent mortality at 65 percent concentration, and 60 percent mortality at 100 percent concentration. The 96 hour LC50 (wastewater strength at which 50 percent of test species survive for 96 hours) was estimated to be 95 percent. The test results are presented in detail in Appendix I.

High ammonia concentrations in Petro-Canada activated sludge plant effluents may be the cause of the toxicity of this wastewater. Esso Refinery activated sludge plant effluent had non-detectable ammonia concentrations and was found to be non-lethal.

TABLE 10: STATISTICAL ANALYSIS OF CONTAMINANT CONCENTRATIONS IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT AT PETRO-CANADA, TRAFALGAR

	SIX INFLUENT 6-HOUR COMPOSITE SAMPLES					SIX EFFLUENT 6-HOUR COMPOSITE SAMPLES					DET. LIMIT
PARAMETERS	FOD	MEAN	MIN	MAX	95% CONFIDENCE RANGE	FOD	MEAN	MIN	MAX	95% CONFIDENCE RANGE	
Conventional											
pH	100	9.6	9.2	9.9	9.3 - 9.9	100	7.4	7.2	7.7	7.1 - 7.6	
Conductivity (umhos/cm)	100	1311	1100	1525	1144 - 1504	100	1397	1200	1580	1222 - 1597	
Alkalinity (mg/L as $CaCO_3$)	100	149	128	157	133 - 166	100	137	79	170	99 - 189	
Suspended Solids (mg/L)	100	57	50	70	49 - 66	100	64	50	80	53 - 78	
Dissolved Organic Carbon (mg/L)	100	45.0	40.3	51.6	40.2 - 50.3	100	17.8	16.0	20.1	16.0 - 19.9	
Ammonia Nitrogen (mg/L)	100	19.2	13.1	25.0	14.3 - 25.7	100	14.7	9.7	20.3	10.6 - 20.2	
Total Kjeldahl Nitrogen (mg/L)	100	21.3	14.8	27.4	16.1 - 28.0	100	19.5	12.4	26.4	13.9 - 27.3	
Nitrate Nitrogen (mg/L)	100	1.02	0.50	2.24	0.5 - 2.2	100	0.34	0.15	0.70	0.2 - 0.7	
Nitrite Nitrogen (mg/L)	100	0.17	0.13	0.25	0.12 - 0.24	0	*	ND	ND	*	0.01
Total Phenols (ug/L)	100	22544	17200	28500	17870 - 28438	100	50.8	36.7	84.3	35.4 - 73.0	
Total Phosphorus (mg/L)	100	0.98	0.36	1.47	0.54 - 1.78	-	-	-	-	-	
Filtered Phosphorus (mg/L)	-	-	-	-	-	50	*	ND	0.68	*	0.15
Oil and Grease (mg/L)†	100	22	12	47	12 - 38	100	21	15	29.2	17 - 29	
Metals (ug/L)											
Arsenic	100	43	24	64	27 - 67	100	44	27	61	31 - 63	1
Cadmium	0	ND	ND	ND	*	0	ND	ND	ND	*	1
Chromium	100	270	180	320	211 - 346	100	280	250	310	247 - 319	1
Copper	100	5	1	11	2 - 15	100	7	1	16	2 - 22	1
Iron	100	1040	700	1420	775 - 1397	100	1298	990	1550	1092 - 1543	30
Lead	100	14	11	20	11 - 18	100	16.3	12	20	13 - 20	1
Mercury	100	0.28	0.20	0.43	0.2 - 0.4	100	0.38	0.12	0.40	0.2 - 0.8	0.05
Nickel	100	6	3	25	2 - 14	100	4	1	16	2 - 13	1
Zinc	100	113	85	150	87 - 145	100	143	130	170	127 - 160	10
Volatile Organic Compounds (ug/L)											
Benzene	100	1540	891	3000	943 - 2515	0	*	ND	ND	*	1.0
Ethylbenzene	100	122	81	177	86 - 172	0	*	ND	ND	*	1.0
Toluene	100	1071	698	1850	732 - 1566	0	*	ND	ND	*	1.0
Xylene	100	584	587	953	542 - 862	0	*	ND	ND	*	1.0
Methylene Chloride**	0	*	ND	ND	*	33	*	ND	13	*	1.0
1,2 Dichloropropane	83	21.8	ND	179	4.2 - 113	50	8.3	ND	41	2.1 - 33	6.0
Chloroform**	17	*	ND	1.8	*	17	*	ND	1.8	*	1.0
Base Neutral Extractable Organic Compounds (ug/L)											
Anthracene	17	*	ND	227	*	0	*	ND	ND	*	1.9
Methyl Anthracene	100	311	235	503	234 - 433	0	*	ND	ND	*	2.0
bis (2-ethylhexyl)phthalate**	83	15	ND	91	2.8 - 82	83	21	ND	120	3.6 - 117	2.5
Di-n-butyl phthalate**	0	*	ND	ND	*	33	*	ND	4.9**	*	2.5
Fluorene	100	94	75	149	69 - 127	0	*	ND	ND	*	1.9
Naphthalene	100	239	189	280	202 - 282	0	*	ND	ND	*	1.6
Methyl Naphthalene	100	2463	2120	2710	2236 - 2713	0	*	ND	ND	*	2.0
Dimethyl Naphthalene	100	2948	2010	3680	2247 - 3868	33	*	ND	12.8	*	2.0
Trimethyl Naphthalene	100	2091	1550	2600	1624 - 2536	33	*	ND	44	*	2.0
Phenanthrene	100	127	54	184	77 - 211	0	*	ND	ND	*	5.4

ND = Not Detected.

FOD = Frequency of detection (percent) above minimum detection limit.

MEAN = Logarithmic mean.

* = Summary statistics not calculated for those parameters that were detected in fewer than one half of samples.

** = Possible contamination.

† = Oil and grease concentrations reported may be higher than actual values (Refer to Appendix F).

Note: Parameters not detected were counted as detects in the statistical analysis and included in the calculations of mean and 95% confidence range as one half of the detection limit.

4.0 DISCUSSION AND INTERPRETATION

4.1 Comparison of Esso Refinery and Petro-Canada Refinery Monitoring Results

There were distinct differences between the natures of the two refineries, the design of the biological systems at the refineries and the operational conditions prevailing at the times of monitoring.

The Esso Refinery is a larger (126,000 barrels per day), more complex, older refinery than the Petro-Canada Refinery (85,000 barrels per day). In terms of the biological treatment plant designs, the Esso Refinery (22,700 m^3/day capacity) utilizes mechanical surface aerators to supply air to uncovered aeration tanks; Petro-Canada (6,019 m^3/day capacity) uses a diffused air system with completely covered aeration tanks. Hydraulic surface loading on the clarifiers at the Esso Refinery (12.7 $m^3/m^2 \cdot$day) was considerably lower than that at the Petro-Canada Refinery (51.0 $m^3/m^2 \cdot$/day).

It is again noted that the Esso activated sludge plant was optimized, whereas the Petro-Canada activated sludge plant was not (refer to Appendix A). During the monitoring periods, the Esso Refinery activated sludge plant was operating at SRTs greater than 30 days, and with dissolved oxygen levels in the aeration tanks averaging 2.3 mg/L. The hydraulic retention time in the aeration tanks averaged 5.6 hours, there was good sludge settleability and nitrification was occurring. At the Petro-Canada Refinery, poor sludge settleability and high clarifier surface loading caused significant suspended solids losses from the final clarifiers, resulting in a short SRT (5.7 days). Dissolved oxygen concentrations in the aeration tanks were typically low, varying between 0.1 and 1.5 mg/L and there was evidence of a phosphorus deficiency. The plant was operating at a total aeration tank HRT of 6.2 hours. There was no evidence that nitrification was occurring in the system.

Biological treatment plant influent concentrations were higher at the Petro-Canada Refinery than at the Esso Refinery in terms of most key conventional contaminants (phenolics, oil and grease, TKN and ammonia), metals and trace organics (volatile aromatic hydrocarbons and PAHs), as illustrated by Table 11. The activated sludge plant at the Esso Refinery is preceded by a biological pretreatment process to reduce influent levels of phenolic compounds upstream of the plant. The dual-media filters at the Esso Refinery

TABLE 11: COMPARISON OF SELECTED INFLUENT AND EFFLUENT CONTAMINANT CONCENTRATIONS FOR ESSO AND PETRO-CANADA

	INFLUENT		EFFLUENT	
	ESSO REFINERY	PETRO-CANADA REFINERY	ESSO REFINERY	PETRO-CANADA REFINERY
Conventional Parameters	(mean)	(mean)	(mean)	(mean)
TKN (mg/L)	11.1	21.3	3.2	19.5
Ammonia (mg/L)	<1	19.2	<1	14.7
Phenols (ug/L)	188	22544	7.7	50.8
Oil and Grease (mg/L)	11.3†	21.5†	6.4†	21.4†
Metals (ug/L)				
As	4	43	5	44
Cd	*	*	*	*
Cr	3	270	3	280
Cu	12	5	8	7
Fe	1023	1040	161	1298
Pb	5	14	3.3	16.3
Hg	0.053	0.28	0.056	0.38
Ni	4	6	5	4
Zn	47	113	32	143
Volatile Aromatic Hydrocarbons	mean (ug/L) (%FOD)	mean (ug/L) (%FOD)	mean (ug/L) (%FOD)	mean (ug/L) (%FOD)
Benzene	73 (83)	1540 (100)	ND (50)	* (0)
Ethylbenzene	4 (50)	122 (100)	* (6)	* (0)
Toluene	27 (83)	1071 (100)	* (11)	* (0)
Xylenes	467 (100)	584 (100)	ND (44)	* (0)
PAH's				
Anthracene	* (0)	* (17)	* (0)	* (0)
Methyl Anthracene	20 (100)	311 (100)	* (0)	* (0)
Acenaphthene	* (17)	* (0)	* (0)	* (0)
Fluorene	* (17)	94 (100)	* (0)	* (0)
Fluoranthene	3 (67)	* (0)	* (0)	* (0)
Naphthalene	* (0)	239 (100)	* (0)	* (0)
Methyl Naphthalene	* (17)	2463 (100)	* (0)	* (0)
Dimethyl Naphthalene	58 (83)	2948 (100)	* (0)	* (33)
Trimethyl Naphthalene	79 (83)	2091 (100)	* (0)	* (33)
Phenanthrene	* (17)	127 (100)	* (0)	* (0)
Pyrene	4 (83)	* (0)	* (0)	* (0)

* No statistical analysis done.

† Oil & grease concentrations reported may be higher than actual values (Refer to Appendix F).

produced lower influent levels of oil and grease than the induced air flotation (IAF) units (that were not operating properly) at the Petro-Canada Refinery. Also, at the Esso Refinery, a regular monitoring of sewers allows source control of wastewater to the activated sludge plant.

Despite these differences in the refineries and their treatment facilities, both biological systems provided a high degree of trace organic contaminant control. No PAH compounds were identified in the effluents from the Esso Refinery activated sludge plant. At the Petro-Canada Refinery, where influent levels of some substituted PAH compounds (methyl, dimethyl and trimethyl naphthalene) were consistently detected in the influents to the activated sludge plant at concentrations more than an order of magnitude higher than at the Esso Refinery, only dimethyl and trimethyl naphthalene were detected in any of the effluent samples. Similarly, both systems effectively reduced the concentrations of volatile aromatic hydrocarbons to near non-detectable levels. In this case, the Petro-Canada Refinery biological treatment system showed better removal efficiency than the Esso Refinery system despite mean influent levels in excess of 1 mg/L. The diffused aeration system at the Petro-Canada Refinery biological plant may have contributed to the higher removal of volatile compounds achieved.

Notable differences were evident in the metal contents of the effluent streams at the two refineries. Influent concentrations of arsenic, chromium, mercury, lead and zinc were significantly higher at the Petro-Canada Refinery than at the Esso Refinery. The higher influent levels produced higher effluent levels for these metals at the Petro-Canada Refinery. No specific source of the higher metals concentrations at the Petro-Canada Refinery was identified.

The most significant differences in quality in the effluents from the two biological systems were evident in three conventional contaminants - ammonia, phenols, and oil and grease. In all three cases, the Esso Refinery biological treatment system produced a better quality effluent than the Petro-Canada Refinery biological treatment system. The longer SRT provided at the Esso Refinery, along with other process conditions condusive to nitrification (higher dissolved oxygen, lower temperature, adequate phosphorus supply), impacted on the removal of nitrogen and may also have contributed to the better performance achieved in terms of effluent phenols concentrations.

4.2 Comparison to Other Studies

In order to validate the analytical results of this study, the results were compared to the findings of other similar monitoring programs. Three previous studies on refinery effluents were examined. Comparison of influent trace contaminant concentrations were not conducted in this review.

The most recent study, conducted by PACE[1] in 1985, was an assessment of the variability of trace organic substances in petroleum refinery effluents. It was based on fifteen 24-hour composite final effluent samples including cooling water (90 percent) storm water (6 percent) and process effluent (4 percent) from one Ontario refinery, over a two month period. An earlier PACE study[2] in 1981 had surveyed seven plants in Canada for trace substances. The data was based on two 12-hour composite samples of final effluent (including biological treatment plant effluent, other contaminated water and possibly cooling water) from each of the seven plants. A third study[3] conducted by the American Petroleum Institute in 1981 evaluated trace contaminants in biological treatment plant effluents at two New Orleans petroleum refineries (referred to as Plant A and Plant B). The results were based on twelve 12-hour composite effluent samples from each refinery collected over a two month period.

Limitations to a direct comparison of the results from these studies should be noted:

- the type, age and complexity of the refineries differed;
- different effluent streams were sampled (i.e. some included cooling water, storm water, as well as biological treatment plant effluent);
- the type of sampling varied between studies (6-hour, 12-hour and 24-hour composite samples);
- analytical procedures used for trace organics analysis have improved since the earlier studies; and
- statistical analyses and presentation of results varied for each study.

Table 12 summarizes the frequency of detection, mean (or median, if mean was unavailable), maximum and minimum concentrations of selected conventional contaminants and all of the metals and trace organics measured in this study.

TABLE 12: SUMMARY OF CONTAMINANT CONCENTRATIONS FOUND IN REFINERY EFFLUENTS IN REVIEWED STUDIES

COMPOUNDS	PRESENT STUDY								PACE (1985)[1]				PACE (1981)[2]				API (1981)[3]							
	ESSO				PETROCANADA												PLANT A				PLANT B			
	FOD	MEAN	MIN	MAX	FOD	MEAN	MIN	MAX	FOD	MEDIAN	MIN	MAX	FOD	MEAN	MIN	MAX	FOD	MEAN	MIN	MAX	FOD	MEAN	MIN	MAX
Conventional Contaminants																								
Suspended Solids (mg/L)	100	8	3	30	100	64	50	80	67	5.1†	ND	18					92	13	ND	77	100	24	6	36
Dissolved Organic Carbon (mg/L)	100	11.3	8.8	15.0	100	17.8	16.0	20.1	87	21†	ND	108	100	44	2	380	100	28	12	81	100	49	32	86
Ammonia Nitrogen (mg/L)	0	*	ND	ND	100	14.7	9.7	20.3	100	0.68†	0.29	0.90	100	6.1	0.1	18.4								
Phenols (ug/L)	100	7.7	4.0	15.4	100	50.8	36.7	84.3	100	36†	9	120	100	2040	2	8800	100	32	9	3760	100	35	11	826
Oil and Grease (mg/L)	100	6.4	4.9	8.7	100	21.4	15.0	29.2	60	3.5†	ND	20	64	7.8	2	24	50	12	ND	26	75	9	ND	73
Metals (ug/L)																								
Arsenic	100	5	3	8	100	44	27	61	20	ND	ND	2	86	6	<2	14	42	*	ND	6	50	14	ND	13
Cadmium	0	*	ND	ND	0	ND	ND	ND					7	1	<2	1								
Chromium	100	3	1	43	100	280	250	310	100	3	1	38	86	190	<2	680	100	75	34	180	100	73	47	240
Copper	100	8	1	180	100	7	1	16					100	13	3	37	8	*	ND	48	0	*	ND	ND
Iron	100	161	77	520	100	1298	990	1550					100	240	2350	600								
Lead	100	3	1	30	100	16	12	20					71	7	<2	180	42	*	ND	3	60	3	ND	9
Mercury	83	0.056	ND	0.20	100	0.38	0.20	0.40					29	0.4	<0.2	0.6								
Nickel	100	5	1	46	100	4	1	16					57	15	<6	38	8	*	ND	7	17	*	ND	9
Zinc	100	32	ND	110	100	143	130	170					100	85	8	240	67	15	ND	110	67	26	ND	160
Volatile Organics (ug/L)																								
Benzene	50	ND	ND	2.5	0	*	ND	ND	100	3	TR	34	50	226	ND	770	50	*	ND	3100	33	*	ND	8
Bromodichloromethanes	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND								
Bromoform	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Bromomethane	0	*	ND	ND	0	*	ND	ND																
Carbon Tetrachloride	0	*	ND	ND	0	*	ND	ND	53	TR	ND	6	29	6.7	ND	20	0	*	ND	ND	0	*	ND	ND
Chlorobenzene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Chloroethane	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
2-Chloroethylvinyl ether	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Chloroform	0	*	ND	ND	17	*	ND	1.8	27	ND	ND	3	79	10.7	ND	26	42	*	ND	236	25	*	ND	6
Chloromethane	0	*	ND	ND	0	*	ND	ND																
bis-Chloromethyl ether	0	*	ND	ND	0	*	ND	ND																
Dibromochloromethane	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Dichlorodifluoromethane	0	*	ND	ND	0	*	ND	ND					0	*	ND	ND	0	*	ND	ND	0	*	ND	ND
1,1-Dichloroethane	0	*	ND	ND	0	*	ND	ND	40	ND	ND	15	14	6.0	ND	9.3	0	*	ND	ND	0	*	ND	ND
1,2-Dichloroethane	0	*	ND	ND	0	*	ND	ND	53	3.7†	ND	18	14	78	16	140	0	*	ND	ND	0	*	ND	ND
1,1-Dichloroethylene	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND
trans-1,2 Dichloroethylene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
1,2-Dichloropropane	0	*	ND	ND	50	8.3	ND	41	53	TR	ND	24	14	9.5	4	15	0	*	ND	ND	0	*	ND	ND
cis-1,3-Dichloropropane	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND								
trans-1,3-Dichloropropane	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND								
Ethylbenzene	6	*	ND	3.4	0	*	ND	ND	33	14†	ND	19	29	7.2	ND	23	17	*	ND	500	0	*	ND	ND
Methylene Chloride	33	*	ND	39	33	*	ND	13	40	ND	ND	6	86	45.1	ND	180								
1,1,2,2-Tetrachloroethene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Toluene	11	*	ND	1.9	0	*	ND	ND	100	3.1†	TR	17	57	208	ND	840	25	*	ND	3500	17	*	ND	4
1,1,1-Trichloroethane	0	*	ND	ND	0	*	ND	ND	40	2.3†	ND	15	36	2.7	ND	5.6	0	*	ND	ND	0	*	ND	ND
1,1,2-Trichloroethane	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Trichloroethylene	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND					0	*	ND	ND	0	*	ND	ND
Trichlorofluoromethane	0	*	ND	ND	0	*	ND	ND					14	5.1	ND	5.3	0	*	ND	ND	0	*	ND	ND
Vinyl Chloride	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Xylenes	44	*	ND	19.5	0	*	ND	ND	67	12	ND	43												
Base-Neutral Extractables (ug/L)																								
Acenaphthene	0	*	ND	ND	0	*	ND	ND	13	ND	ND	TR	7	TR	TR	TR	25	*	ND	10	0	*	ND	ND
Acenaphthylene	0	*	ND	ND	0	*	ND	ND	13	ND	ND	TR	7	TR	TR	TR	0	*	ND	ND	0	*	ND	ND
Anthracene	0	*	ND	ND	0	*	ND	ND	6	ND	ND	TR	14	0.13	ND	0.25	0	*	ND	ND	8	*	ND	1
Methyl anthracene	0	*	ND	ND	0	*	ND	ND	47	ND	ND	10												
bis (2-chloroethoxyl) methane	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
bis (2-chlorethyl) ether	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
bis (2-chloroisopropyl) ether	0	*	ND	ND	0	*	ND	ND					7	37	ND	37	0	*	ND	ND	0	*	ND	ND
bis (2-ethylhexyl) phthalate	89	11	ND	78	83	21	ND	120					29	11.1	ND	14.4	92	10	ND	100	83	8	ND	200
Benzidine	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Benzo(a)anthracene	0	*	ND	ND	0	*	ND	ND					21	4.2	ND	9.0	67	*	ND	4	41	*	ND	1
Benzo(a)pyrene	0	*	ND	ND	0	*	ND	ND					0	*	ND	ND	0	*	ND	ND	0	*	ND	ND
Benzo(b)fluoranthene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Benzo(g,h,i)perylene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Benzo(k)fluoranthene	0	*	ND	ND	0	*	ND	ND	0	*	ND	ND	29	0.10	ND	0.1	0	*	ND	ND	0	*	ND	ND
Butyl Benzylphthalate	0	*	ND	ND	0	*	ND	ND	67	TR	ND	TR	0	*	ND	ND	25	*	ND	1	17	*	ND	1
Chrysene	0	*	ND	ND	0	*	ND	ND	67	1.1†	ND	9	29	1.3	ND	2.8	67	*	ND	4	41	*	ND	1
Di-n-butylphthalate	28	*	ND	10.1	33	*	ND	4.9	100	7	TR	56	7	TR	ND	TR	83	1	ND	6	67	1	ND	6
Di-n-octylphthalate	6	*	ND	3.7	0	*	ND	ND	100	11	TR	154	0	*	ND	ND	25	*	ND	8	25	*	ND	2
Dibenzo(a,h)anthracene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Diethylphthalate	39	*	ND	4.9	0	*	ND	ND	47	ND	ND	2	14	16.5	ND	21	58	3	ND	85	53	3	ND	94
Dimethylphthalate	0	*	ND	ND	0	*	ND	ND	27	ND	ND	TR	7	14	ND	ND	8	*	ND	2	0			
Fluoranthene	0	*	ND	ND	0	*	ND	ND	6	ND	ND	TR	0	*	ND	ND	8	*	ND	1	0	*	ND	ND
Fluorene	0	*	ND	ND	0	*	ND	ND	60	TR	ND	TR	21	2.4	ND	5.1	17	*	ND	6	0	*	ND	ND
Hexachlorobenzene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Hexachlorobutadiene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Hexachloroethane	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Indeno(1,2,3-c,d)pyrene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Isophorone	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
N-nitrosodiphenylamine	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
Naphthalene	0	*	ND	ND	0	*	ND	ND	80	4.6†	ND	69	57	7.3	ND	3.2	6	*	ND	11	8	*	ND	1
Methyl Napthalene	0	*	ND	ND	0	*	ND	ND																
Dimethyl Naphthalene	0	*	ND	ND	33	*	ND	12.8	67	TR	ND	65												
Trimethyl Napthalene	0	*	ND	ND	33	*	ND	44																
Nitrobenzene	0	*	ND	ND	0	*	ND	ND																
Phenanthrene	0	*	ND	ND	0	*	ND	ND	40	1.0†	ND	3	29	3.6	ND	13	0	*	ND	ND	0	*	ND	ND
Pyrene	0	*	ND	ND	0	*	ND	ND	33	ND	ND	2	36	0.9	ND	1.6	25	*	ND	ND	8	*	ND	1
1,2,4-Trichlorobenzene	0	*	ND	ND	0	*	ND	ND									50	*	*	3	33	*	ND	1
1,2-Dichlorobenzene	0	*	ND	ND	0	*	ND	ND																
1,3-Dichlorobenzene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
1,4-Dichlorobenzene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
2,4-Dinitrotoluene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
2,6-Dinitrotoluene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
2,-chloronaphthalene	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
3,3'-Dichlorobenzidine	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
4-Bromophenyl phenyl ether	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND
4-chlorophenyl phenyl ether	0	*	ND	ND	0	*	ND	ND									0	*	ND	ND	0	*	ND	ND

* = No statistical analysis done.

ND = Not Detected

TR = Trace (<2 ug/L)

† = Logarithmic mean.

1 - PACE (1985): Based on fifteen 24-hour composite final effluent samples, including cooling water (90%), stormwater (6%) and process effluent (4%) from one Ontario refinery after a two month period.

2 - PACE (1981): Based on two 12-hour composite samplers of final effluent (including biological treatment effluent, other contaminated waters and possibly cooling waters) from seven Ontario refineries.

3 - API (1981): Based on twelve biologically treated effluent samples from two New Orleans area refineries.

In terms of trace contaminants (metals and organics), metals were frequently detected in all studies in which they were analyzed. Chromium was most commonly reported in all studies. Zinc was also reported with a frequency of detection higher than 50 percent in all studies in which it was analyzed.

There were no trace organics (volatile compounds or base-neutral compounds) that were reported at a frequency of detection higher than 50 percent in all studies. The volatile aromatic hydrocarbons benzene, toluene and xylenes were most frequently reported although xylenes were not analyzed for in the early PACE study[2] or the API study[3]. Ethylbenzene, methylene chloride, 1,2-dichloropropane and chloroform were commonly reported in all studies. Phthalate esters, particularly bis (2-ethylhexyl) phthalate, were the most commonly reported base-neutral extractable compounds. Similar to this study, phthalate esters were found in other studies at concentrations of up to 200 ug/L for bis (2-ethylhexyl) phthalate[3]. Also, in one study[3], phthalate esters were found in most laboratory blanks, causing reason to suspect that their presence was a result of contamination. Fewer PAH compounds were detected in this study than in the previous reported studies.

Table 13 identifies the trace organic contaminants that were detected and in which study they were detected. Volatile organic compounds that were detected in all of the studies (in which they were analyzed) included benzene, chloroform, 1,2 dichloropropane, ethylbenzene, methylene chloride, toluene, and xylenes. Base-neutral extractable organics that were identified in all of the studies (in which they were analyzed) included phthalate esters [bis-(2-ethylhexyl) phthalate, di-n-butylphthalate, diethylphthalate] and dimethyl naphthalene.

Table 14 identifies those trace organic compounds that were not detected in any study (in which they were analyzed. The list of non-detected compounds is more extensive than the list of detected compounds.

4.3 Identification of a Surrogate Parameter to Indicate Trace Contaminant Removal

In this context, a surrogate parameter is a parameter or group of parameters that can be used as an indicator of the presence or absence of trace contaminants in an effluent. Identification of a readily measurable surrogate, which could provide a rapid, inexpensive indication of effluent

TABLE 13: SUMMARY OF TRACE ORGANIC CONTAMINANT DETECTION IN REVIEWED STUDIES

COMPOUND	STUDY IN WHICH COMPOUND WAS DETECTED:			
	PRESENT	1	2	3
Volatiles				
Benzene	x	x	x	x
Carbon Tetrachloride		x	x	
Chloroform	x	x	x	x
1,1 Dichloroethane		x	x	
1,2 Dichloroethane		x	x	
1,2 Dichloropropane	x	x	x	
Ethylbenzene	x	x	x	x
Methylene Chloride	x	x	x	NM
Toluene	x	x	x	x
1,1,1 Trichloroethane		x	x	
Trichlorofluoromethane		NM	x	
Xylenes	x	x	NM	NM
Base Neutrals				
Acenaphthene		x	x	x
Acenaphthylene		x	x	
Anthracene		x	x	x
Methyl Anthracene		x	NM	NM
bis (2-chloroisopropyl) ether			x	
bis (2-ethylhexyl)phthalate	x	NM	x	x
Benzo(a)anthracene		NM	x	x
Benzo(k)fluoranthene			x	
Butyl Benzylphthalate		x		x
Chrysene		x	x	x
Di-n-butylphthalate	x	x	x	x
Di-n-octylphthalate	x	x		x
Diethylphthalate	x	x	x	x
Fluorene		x	x	x
Naphthalene		x	x	x
Dimethyl Naphthalene	x	x	NM	NM
Trimethyl Naphthalene	x	NM	NM	NM
Phenanthrene		NM	x	x
Pyrene		x	x	x

NM = Not measured

1 - PACE (1985) : Based on fifteen 24-hour composite final effluent samples, including cooling water (90%), stormwater (6%) and process effluent (4%), from one refinery over a 2 month period.

2 - PACE (1981) : Based on two 12-hour composite samples of final effluent (includes biological treatment effluent, other contaminated waters and possibly cooling water) from 7 Ontario refineries.

3 - API (1981) : Based on 12 composite effluent samples from biologically treated effluents at two New Orleans area petroleum refineries.

TABLE 14: TRACE ORGANICS NOT DETECTED IN PRESENT OR PREVIOUS STUDIES OF REFINERY EFFLUENTS

PURGEABLE ORGANICS	BASE NEUTRAL ORGANICS
Bromodichloromethane	bis (2-chloroethyxyl)methane[1,2]
Bromoform[1,2]	bis (2-chloroethyl) ether[1,2]
Bromomethane[1,2]	Benzidine[1,2]
Chlorobenzene[1,2]	Benzo(a)pyrene[1]
Chloroethane[1,2]	Benzo(b)fluoranthene[1,2]
2-Chloroethylvinyl ether[1,2]	Benzo(g,h,i)perylene[1,2]
Chloromethane[1,2,3]	Dibenzo(a,h)anthracene[1,2]
bis-Chloromethyl ether[1,2,3]	Diethylphthalate[1,2]
Dibromochloromethane[1,2]	Dimethylphthalate[1,2]
Dichlorodifluoromethane[1]	Hexachlorobenzene[1,2]
1,1-Dichloroethylene	Hexachlorobutadiene[1,2]
trans-1,2-Dichloroethyl	Hexachlorethane[1,2]
cis-1,3-Dichloropropene	Indeno(1,2,-c,d)pyrene[1,2]
trans-1,3-Dichloropropene[1,2]	Isophorone[1,2]
1,1,2,2-Tetrachloroethane[1,2]	N-nitrosodiphenylamine[1,2]
1,1,2,2-Tetrachloroethene	Nitrobenzene[1,2]
1,1,2-Trichloroethane[1,2]	1,2,4-Trichlorobenzene[1,2]
Trichloroethylene[2]	1,2-Dichlorobenzene[1,2]
Vinyl Chloride	1,3-Dichlorobenzene[1,2]
	1,4-Dichlorobenzene[1,2]
	2,4-Dinitrotoluene[1,2]
	2,6-Dinitrotoluene[1,2]
	2-chloronephthalene[1,2]
	3,3'-Dichlorobenzidine[1,2]
	4-Bromophenyl phenyl ether[1,2]
	4-chlorophenyl phenyl ether[1,2]

1. Not analyzed for Study 1
2. Not analyzed for Study 2
3. Not analyzed for Study 3

quality in terms of trace contaminants, would have significant benefits from the standpoint of process control as well as cost. Ideally, a surrogate must be a positive indicator of the presence and absence of trace contaminants. In the selection of an effective surrogate, erroneous indication of the presence of trace contaminants is preferred to the erroneous indication of the absence of trace contaminants.

A variety of non-specific conventional contaminants such as COD, TOC and phenolic compounds have been suggested as surrogate measures of trace contaminant concentrations. Specific trace contaminants, such as benzene, toluene, or xylene, might also serve as surrogates in refinery wastewaters. It has also been suggested[4] that the presence of nitrification, as indicated by ammonia conversion to nitrate in the biological system, might serve as a surrogate measure of effective trace contaminant control since nitrifiers are sensitive to the presence of inhibitory trace contaminants. Furthermore, nitrification requires stable biological process operation at relatively long SRT's which normally produce a high degree of trace organic removal.

The results of this investigation showed that both biological treatment systems achieved a high level of trace organic contaminant control, despite significant differences in process operations. One plant was operated at high SRT (>30 days) and achieved nitrification, whereas the other plant was operated at a relatively low SRT (5 days) and did not nitrify. One plant received a lower strength, pretreated wastewater which was lower in phenolic compounds, nitrogenous compounds and trace organics than the other plant. One plant achieved significantly lower effluent phenol concentrations than the other plant.

Establishing a surrogate parameter requires that there are measurable differences in effluent quality in terms of trace compounds which can be correlated to changes in another parameter such as TOC, phenols or nitrogen. In this particular case, there was not sufficient variation in the concentration of any of the trace contaminants to allow the identification of a surrogate parameter. The data indicate, for example, that trace contaminant concentrations were low when effluent phenol concentrations were less than 100 ug/L and phenol removal efficiency exceeded 95 percent. However, the data

provides no indication of whether a higher phenol concentration in the effluent would correspond to the presence of significant levels of trace contaminants. This finding is consistent with the API study. Benzene was the most commonly detected non-phthalate ester in Esso Refinery effluents, but was not detected in effluents from the Petro-Canada Refinery which did contain other trace organics.

Other studies[4] have indicated that in some complex industrial wastewaters, the presence of nitrification could be used as an effective surrogate indicator of trace contaminant removal. In this study, the nitrifying system produced effluent phenol concentrations significantly lower than the non-nitrifying system. Therefore, although the results of this study cannot be used to confirm the appropriateness of nitrification as surrogate, it does provide evidence that the presence of nitrification in the biological system is an indicator of efficient stable, process operation.

5.0 CONCLUSIONS

The sampling and analysis program was conducted in order to meet three objectives: to determine the relationship between effluent trace contaminant concentrations and biological treatment plant and refinery operation, to assess the practicability of selecting a surrogate parameter for identification of trace contaminant removal, and to validate previous studies on trace contaminants in refinery effluents.

The following conclusions have been drawn from the results of the monitoring program:

1. **The biological treatment plants at both refineries studied demonstrated highly efficient removal of trace organic contaminants.** The only trace organic detected in effluents from both refineries at a frequency greater than 50 percent were phthalate esters which were also present in field blank samples and may have been associated with laboratory or field contamination. Volatile aromatic compounds were identified up to 50 percent of the time [benzene (50%), xylenes (44%), toluene (11%) and ethylbenzene (6%)] at near detection limit concentrations in Esso Refinery effluents and were not detected in Petro-Canada Refinery effluents. Polynuclear aromatic hydrocarbons (PAHs) were not detected in any Esso Refinery effluent samples. At Petro-Canada Refinery, two substituted PAH compounds (dimethyl and trimethyl naphthalene) were detected in 33 percent of the effluent samples.
2. **Effluent quality was similar at both refineries with respect to trace organic contaminants** despite significant differences in refinery size and complexity, biological treatment plant design and operation, and influent quality.
3. **Differences in effluent quality at the two refineries was in the concentrations of conventional contaminants** (suspended solids, phenols, total TKN and ammonia nitrogen) **and metals.** The biological treatment plant which had lower influent phenol concentrations and was nitrifying produced lower effluent phenol concentrations than the plant which was not nitrifying and had relatively high influent phenol concentrations.

4. Because effluent quality in terms of trace organics was similar at both refineries and concentrations were near the detection limits of the analytical methods, **no relationship could be identified between trace organic removal performance in the biological treatment plant and the operating conditions in the refinery or biological treatment plant.**

5. **The results generated from this monitoring program were consistent with those reported in previous studies of petroleum refinery effluents.** In general, fewer volatile and base neutral extractable organics were detected, at lower concentrations and at a lower frequency of detection in the present study than in previous studies.

6. **A surrogate parameter which would be an indicator of trace contaminant concentrations in effluents could not be identified from the results of this study.** Trace organic contaminants were typically not detected in effluents from either refinery. Further, there was little variability in the concentrations of conventional contaminants in effluents from either refinery over the range of conditions encountered.

   To identify a surrogate parameter indicative of effluent quality, controlled studies at pilot scale over a wider range of trace contaminants concentrations than normally found in refinery biotreater effluent would be required.

   Since the results of this investigation support the findings of previous studies, further full-scale monitoring programs for surrogates on petroleum refinery effluents are not considered warranted.

6.0 REFERENCES

1. "Evaluation of the Variability of Trace Organic Substances in Petroleum Refinery Effluents". Report prepared for Petroleum Association of Conservation of the Canadian Environment, PACE Report No. 85-7, Ottawa, Ontario.

2. "Survey of Trace Substances in Canadian Petroleum Industry Effluents". Report prepared for Petroleum Association for Conservation of the Canadian Environment, PACE Report No. 81-4, Ottawa, Ontario.

3. "Refinery Wastewater Priority Pollutant Study - Sample Analysis and Evaluation of Data", 1981 Publication No. 4346. American Petroleum Institute, Washington, D.C.

4. Melcer, H. and Nutt, S.G., "The Application of Predentitrification Nitrification Technology for Trace Contaminant Control", Water Sci. Tech., 17, 339, (1984).

5. American Public Health Assoc. (APHA), 1985. "Standard Methods for the Examination of Water and Wastewater", 16th Edition, APHA, Washington, D.C.

APPENDIX A

REFINERY SELECTION

APPENDIX A - REFINERY SELECTION

Selection of two refineries of the six in Ontario for inclusion within this two-plant trace contaminant study was completed by the Project Steering Committee which consisted of members from provincial government, federal government and industry. The selection was based on a review of both specific features of the plant and previous characterization work. Specific considerations of the plant sites selected are listed below:

Esso Petroleum Canada - Sarnia Refinery

- Oldest refinery in the province.
- Representative of the largest.
- Representative of the most complex with respect to the variety of refining processes on-site.
- Wastewater treatment facilities for the most part conventional without any tertiary treatment.
- Operation of the wastewater treatment system is relatively optimized with respect to nitrification and extended solids retention time (SRT).

Petro-Canada - Trafalgar Refinery

- Smaller refinery.
- Relatively simple cracking type refinery.
- Wastewater treatment facilities are conventional with minimal tertiary treatment (polishing pond) (sampling was before the polishing pond).
- Operation of the wastewater treatment system is not considered optimized at this time with respect to SRT or nitrification.

Sites eliminated included two new refineries and two medium sized cracking refineries.

Texaco - Nanticoke

- New refinery.
- Characterization studies indicate minimal trace contaminants in effluent wastewaters.

Petrosar - Corunna

- New petrochemical refinery.

Shell - Corunna

- Medium sized cracking refinery.
- Unavailable for analysis due to shutdown schedule.

Suncor - Sarnia

- Medium sized cracking refinery.
- Potential contamination of intake waters with trace organics.

APPENDIX B

SAMPLING METHODOLOGY

APPENDIX B - SAMPLING METHODOLOGY

All activated sludge plant influent and effluent samples, and Esso Refinery service water samples were collected each hour of the six hour sampling period in either glass or stainless steel containers. Each individual aliquot volume was composited and preserved in the sample container at each hourly interval, with the exception of the samples for volatile organic compounds and oil and grease analysis. Sample aliquots for volatile organic compounds analysis were stored and preserved in individual vials each hour and composited immediately before laboratory analysis. Oil and grease sample aliquots were put directly into containers that were premarked for the required volume. Sample liquid was filled to the mark and the six hourly aliquots were not composited until immediately before analysis. Sample containers were solvent rinsed to include any oil and grease adhering to the container. All samples were refrigerated in the field, and were kept refrigerated until analysis.

Table B-1 presents the sample preservation methods and type of sample container used for each of the parameters.

TABLE B-1: SUMMARY OF SAMPLE HANDLING METHODS

PARAMETER	SAMPLE CONTAINER	PRESERVATION
pH	P	-Analyzed on-site
Conductivity	P	-Analyzed on-site
Alkalinity	P	-Refrigerate
Suspended Solids	P	-Refrigerate
Dissolved Organic Carbon (DOC)	G	-Filtered on-site -H_2SO_4 (pH <2) -Refrigerate
Ammonia Nitrogen	G	-H_2SO_4 (pH <2) -Refrigerate
Total Kjeldahl Nitrogen	G	-H_2SO_4 (pH <2) -Refrigerate
Nitrate Nitrogen	G	-H_2SO_4 (pH <2) -Refrigerate
Nitrite Nitrogen	G	-Refrigerate
Phosphorus	G (HCl wash)	-Filt. P - Filtered on-site -Refrigerate
Total Phenols	G	-H_2SO_4 (pH <2) -Refrigerate
Oil and Grease	G	-H_2SO_4 (pH <2) -Refrigerate
Metals	G (HNO_3 wash)	-HNO_3 (pH <2) -Refrigerate
Purgeables	G, Teflon - capped	-Sodium Thiosulphate (80 mg/L) -Refrigerate
Base-Neutral Extractables (PAHs)	G (organic solvent wash)	-Sodium Thiosulphate (80 mg/L) -Refrigerate

G = Glass P = Plastic

APPENDIX C

ANALYTICAL METHODS

APPENDIX C - ANALYTICAL METHODS

C-1 Conventional Contaminants

The analytical methodologies that were applied for conventional contaminant analysis are stated in Table C-1.

TABLE C-1: SUMMARY OF ANALYTICAL PROCEDURES

DETERMINATION	METHOD*	MINIMUM DETECTION LIMIT
Alkalinity	Titration & Electrochemical measurement	20 mg/L as $CaCO_3$
Suspended Solids	Glass Fibre Filter	Depends on Vol. Filtered
Conductivity	Conductivity Cell	1 umho/cm
Dissolved Organic Carbon	Astro Model 2001 TOC Analyzer	4 ug/L
Ammonia Nitrogen	1 Distillation & Nesslerization Method	1.0 mg/L
	2 Specific Ion Electrod method	0.01 mg/L
Total Phenols	4 - AAP with Chloroform Extraction	1 ug/L
Oil and Grease	Trichlorotrifluoroethane Extraction, Gravimetric method	5 mg/L
Nitrate Nitrogen	Chromotropic Acid	0.01 mg/L
Nitrite Nitrogen	Diazotization Method	0.01 mg/L
Phosphorus	Vanadomolybdophosphoric Acid	0.15 mg/L
Kjeldahl Nitrogen	Macro	1.0 mg/L

* From APHA (16th Ed)[5]

C-2 Metals

Total metals were analyzed after sample digestion using the following methods. The direct flame Atomic Absorption Spectrophotometer (AA) was used for the analysis of Fe and Zn and high levels of Cd, Cu, Cr, Pb and Ni. Low levels of Cd, Cu, Cr, Pb and Ni were analyzed using the graphite furnace AA. Arsenic was analyzed using the hydride generation AA, and Hg was analyzed using the cold vapour AA.

In addition, as a further check on quality, Fe, Zn, Cd, Cr, Pb and Ni were analyzed by Inductively Coupled Plasma (ICP) Spectrometry. Detection limits are presented in Table C-2 for the AA and ICP methodologies. The instruments used for metal analyses are listed in Table C-3.

TABLE C-2: DETECTION LIMITS FOR TRACE METAL ANALYSES

	DIRECT AA (mg/L)	GRAPHITE AA (mg/L)	ICP (mg/L)	HYDRID (mg/L)	COLD VAPOUR (mg/L)
Iron	0.05	0.001	0.030	-	-
Zinc	0.01	0.001	0.015	-	-
Cadmium	0.01	0.001	0.025	-	-
Chromium	0.05	0.001	0.030	-	-
Copper	0.01	0.001	0.15	-	-
Lead	0.1	0.001	0.08	-	-
Nickel	0.05	0.001	0.025	-	-
Arsenic	-	-	-	0.001	-
Mercury	-	-	-	-	0.00005

TABLE C-3: INSTRUMENTS USED FOR ANALYSIS OF METALS

INSTRUMENT	M O D E L
Direct AA	Varian Model 475
Graphite AA	Perkin Elmer Model 603 with MHS-1 System
ICP	Jarrell Ash Model 975, equipped with a Minipuls 2 Peristaltic Pump, and an all glass MAK High Pressure Nebulizer
Hydride	Perkin Elmer Model 603 with MHS-1 System
Cold Vapour	Pharmacia Mercury Monitor Model 100 M

C-3 Volatile Organic Compounds

Samples for volatile organic compound analysis were received by CAN TEST within 24 hours of sampling and were analyzed within the recommended 72-hour period after sampling. Inside a cold room (4°C), the contents of the six vials were combined in a beaker to form one composited sample. After mixing the composited water, the sample was tranferred to pre-cleaned and labelled purge vials pending analysis. The EPA Method 624 (GC/MS)[6] was utilized for the analysis. This method covers the determination of the volatile organic compounds defined by the EPA Priority Pollutant List. These compounds (and their corresponding detection limits) are listed in Table C-4. The actual analysis is based on a purge and trap gas chromatographic/mass spectrometer (GC/MS) method.

In summary, an inert gas was bubbled through a 5 mL sample contained in a specifically designed purging chamber (Teckmar Purging Apparatus) at ambient temperatures. The vapour was swept through a sorbent column where the volatile organic compounds were trapped. The sorbent column was then heated to 30°C and backflushed with an inert gas for 8 minutes at 180°C to desorb the volatile organic compounds into a gas chromatograph column. The gas chromatograph, with settings listed in Table C-5, was temperature programmed to separate volatile organic compounds, which were then detected with a mass spectrophotometer.

An internal standard of 0.2 ug of bromofluorobenzene in 5 mL of reagent water was added to each sample inside the purging apparatus so that key mass spectra (m/z) abundance criteria met the standard set out by EPA method 624. To monitor the analytical variability of the method, deuterated compounds of some of the parameters of interest were added to each sample as surrogate standards. The details of this procedure are discussed in Appendix D.

The instruments used in this method were the Tekmar-LSC-2 Purge and Trap Apparatus and the OWA-1020 Gas Chromatograph/Mass Spectophotometer equipped with a 1% SP1000 6/80 mesh Carbopack B column.

TABLE C-4: DETECTION LIMIT FOR VOLATILE ORGANIC COMPOUNDS

COMPOUND	DETECTION LIMIT (ug/L)
Benzene	1.0
Bromodichloromethane	2.2
4-Bromofluorobenzene*	7.5
Bromoform	4.7
Bromomethane	3.5
Carbon Tetrachloride	2.8
Chlorobenzene	6.0
Chloroethane	1.5
2-Chloroethylvinyl Ether	8.0
Chloroform	1.6
Chloromethane	2.0
bis-Chloromethyl Ether	3.1
Dibromochloromethane	4.0
Dichlorodifluoromethane	4.7
1,1-Dichloroethane	2.8
1,2-Dichloroethane	2.8
1,1-Dichloroethylene	1.6
trans-1,2-Dichloroethylene	6.0
1,2-Dichloropropane	5.0
cis-1,3-Dichloropropene	5.0
1,2-Dichloropropylene	6.0
Ethylbenzene	1.0
Methylene Chloride	2.8
1,1,2,2-Tetrachloroethane	6.9
1,1,2,2-Tetrachloroethene	4.1
Toluene	1.0
1,1,1-Trichloroethane	3.8
1,1,2-Trichloroethane	5.0
Trichloroethylene	1.9
Trichlorofluoromethane	2.0
Vinyl Chloride	2.0
Xylene (o,p,m)	1.0

* Internal Standard

TABLE C-5: GAS CHROMATOGRAPH CONDITIONS FOR VOLATILE ORGANIC COMPOUND ANALYSIS

PARAMETER	SETTING
Injection Temperature	230°C
Oven Temperature	30 - 230°C @ 8 c/n
Transfer Line Interface	230°C
Flowrate	30 mL/min
Purge Rate	40 mL/min from a Teckmar LSC-2

C-4 Base Neutral Extractable Organic Compounds

The EPA Method 625[6] was utilized for the analysis of base neutral extractable organic compounds. This method covers the determination of base neutral extractable organic compounds defined by the EPA priority pollutant list. These compounds and their corresponding detection limits are listed in Table C-6.

In summary, 1 L of sample was put into a 2 L separatory funnel. The pH was adjusted to 12 with sodium hydroxide and the sample was extracted three times with 100 mL methylene chloride. The methylene chloride extract was passed through a sodium sulphate anhydrous column, and evaporated to approximately 5 mL at 65°C using a Kuderna-Danish (KD) flask (with a 3-ball snyder column and a 10 mL concentration tube). The KD flask was removed, and a 2-ball micro-snyder column was attached. The extract was then further evaporated to 1 mL and cooled. The deuterated standard compounds were added (refer to Appendix D) and the final volume was adjusted to 2 mL. The extract was stoppered and refrigerated until GC/MS analysis.

Using the GC conditions listed in Table C-7, gas chromatograph/mass spectrometer analysis was performed. The internal standard, decafluorotriphenylphosphine (DFTPP), was added to the sample before analysis and mixed immediately. 2 uL of sample extract was injected into the GC/MS system using the spitless injection technique.

TABLE C-6: DETECTION LIMIT FOR BASE NEUTRAL EXTRACTABLE ORGANIC COMPOUNDS

COMPOUND	DETECTION LIMIT (ug/L)
Acenaphthene	1.9
Acenaphthylene	3.5
Anthracene	1.9
Methyl Anthracene	2.0
bis-(2-chloroethexyl) methane	5.3
bis-(2-chloroethyl)ether	5.7
bis-(2-chloroisopropyl)ether	5.7
bis-(2-ethylhexyl)phthalate	2.5
Benzidine	44
Benzo(a)anthracene	7.8
Benzo(a)pyrene	2.5
Benzo(b)fluoranthene	4.8
Benzo(g,h,i)perylene	4.1
Benzo(k)fluoranethene	2.5
Butyl Benzylphthalate	2.5
Chrysene	2.5
Di-n-butylphthalate	2.5
Di-n-octylphthalate	2.5
Dibenzo(a,h)anthracene	2.5
Diethylphthalate	2.5
Dimethylphthalate	1.6
Fluoranthene	2.2
Fluorene	1.9
Hexachlorobenzene	1.9
Hexachlorobutadiene	.9
Hexachloroethane	1.6
Indeno(1,2,3-c,d)pyrene	3.7
Isophorone	2.2
n-Nitrosodiphenylamine	1.9
Naphthalene	1.6
Nitrobenzene	1.9
Phenanthrene	5.4
Pyrene	1.9
Methyl Naphthalene	2.0
Dimethyl Naphthalene	2.0
Trimethyl Naphthalene	2.0
1,2,4-Trichlorobenzene	1.9
1,2-Dichlorobenzene	1.9
1,3-Dichlorobenzene	1.9
1,4-Dichlorobenzene	4.4
2,4-Dinitrotoluene	5.7
2,6-Dinitrotoluene	1.9
2-Chloronaphthalene	1.9
3,3-Dichlorobenzidine	16.5
4-Bromophenyl Phenyl Ether	1.9
4-Chlorophenyl Phenyl Ether	4.2

TABLE C-7: GAS CHROMATOGRAPH CONDITIONS FOR BASE NEUTRAL EXTRACTABLE ORGANIC COMPOUND ANALYSIS

PARAMETER	SETTING
Injection Temperature	280°C
Oven Temperature	30 - 280°C @ 7 c/n
Transfer Line Interface	260°C
Flowrate	5 cm/sec

The instrument used in this method was the Finnigan OWA-1020 Gas Chromatograph/Mass Spectrometer equipped with a SPB-5 30 meter column by auto-quantitation software data system, recommended by EPA[6] for organic priority pollutant analysis.

APPENDIX D

QA/QC PROGRAM METHODOLOGY

APPENDIX D - QA/QC PROGRAM METHODOLOGY

All analytical procedures (conventionals, metal and trace organics) were included in the following QA/QC program:

i) Field Blanks

A "field blank" case of bottles, filled with distilled water, was shipped to the sampling site along with all of the sample bottles for the site. At the end of the sampling period, each container of the field blank was opened and sufficient water poured out to leave a volume of water in the bottle equivalent to a 6-hour composite sample. Open containers were carried out to the sampling locations. Volumes of preservative identical to that used for the samples were added and the bottles re-sealed for shipment with the actual samples.

ii) Laboratory (Method) Blanks

A "method blank" (i.e. a volume of de-ionized, distilled laboratory water) was carried through the entire analytical procedure.

Method blank analyses were performed at the following frequency:

- For the analysis of conventional contaminants, a method blank was performed with every ten (10) samples or at least once per day.
- For the analysis of volatile organic comounds, a method blank analysis was performed every twelve hours, or with every ten (10) samples of similar concentration and/or sample matrix, whichever was more frequent.
- For the analysis of base neutral extractable organic compounds, a method blank analysis was performed with every ten (10) samples of similar concentration and/or sample matrix or whenever samples were extracted by the same procedure. The method blank associated with a specific set or group of samples was analyzed on each GC/MS system used to analyze that specified group or set of samples.

iii) Duplicate

From each set of 6 samples, one sample was selected at random for duplicate analysis.

iv) MOE QA/QC Program

On one day during one sampling period at each refinery, effluent samples were collected, composited, preserved and refrigerated in prepared and labelled containers supplied by MOE. These samples were shipped the following day to the MOE laboratory for analysis. Field blank and sample results were compared to results obtained by CANVIRO and CAN TEST for that day to further verify analytical and field procedures.

In addition to the above, the QA/QC program for metals consisted of analysis of every sample in duplicate, and analysis of EPA reference samples. All instrumentation (AA, Hydride, Cold Vapour, ICP) was calibrated each day with synthetic standards prepared in the laboratory and the accuracy of the calibration was checked with EPA reference samples.

The accuracy and precision of the volatile organic compounds was monitored as an additional step in the QA/QC program. The following deuterated surrogate standards were used:

Toluene - d8
1,2-Dichloroethane - d4

Similarly, for the base neutral extractable organics analyses, the following deuterated surrogate standards were used:

Chrysene - d12
Naphthalene - d8
Phenanthrene - d10

Surrogate standard determinations were performed on all samples and blanks. All samples and blanks were fortified with surrogate spiking compounds before purging or extraction in order to monitor preparation and

analysis of samples. Surrogate spike recovery was evaluated for acceptance by determination whether the concentration (measured as percent recovery) fell into the internally prescribed recovery limits listed in Table D-1.

TABLE D-1: SURROGATE SPIKE RECOVERY LIMITS

FRACTION	SURROGATE COMPOUND	RECOVERY RANGE
VOA	Toluene - d8	88 - 110
VOA	1,2-Dichloroethane - d4	76 - 114
BN	Chrysene - d12	40 - 130
BN	Naphthalene - d8	35 - 119
BN	Phenanthrene - d10	65 - 128

APPENDIX E

LOG NORMAL PROBABILITY PLOTS OF SELECTED PARAMETERS IN ESSO REFINERY ACTIVATED SLUDGE PLANT EFFLUENT

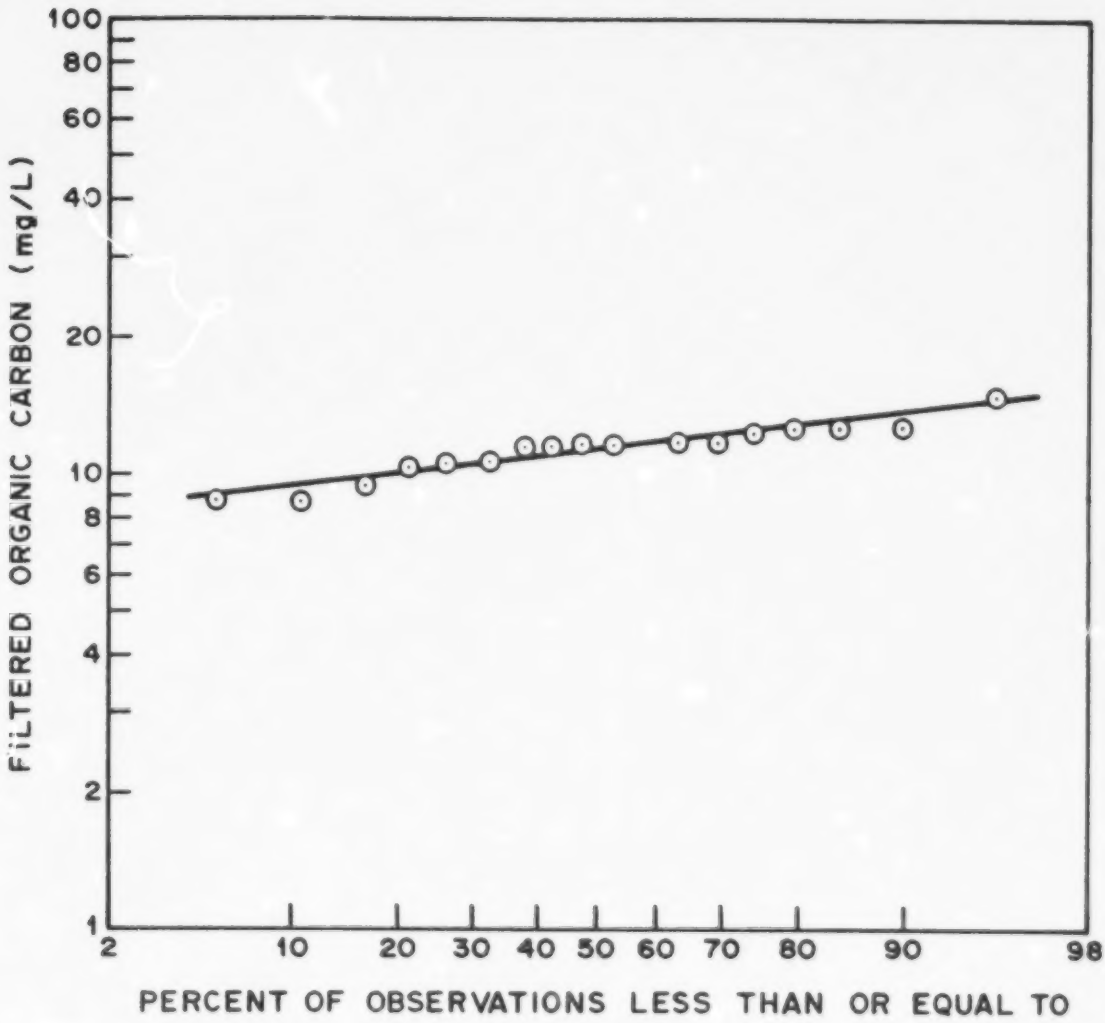

FIGURE E-1 LOG NORMAL PROBABILITY PLOT OF DISSOLVED ORGANIC CARBON IN ACTIVATED SLUDGE PLANT EFFLUENT AT ESSO REFINERY

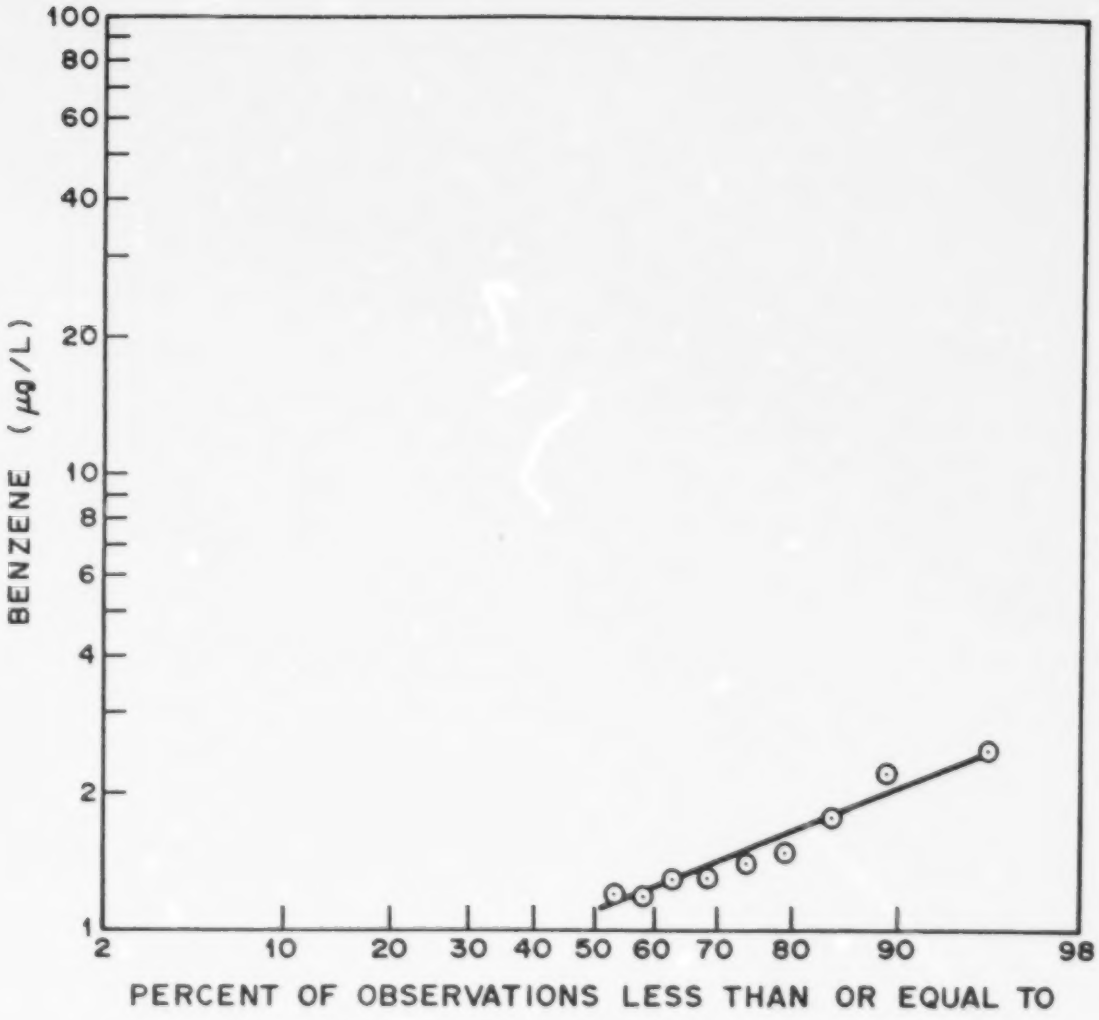

FIGURE E-2 LOG NORMAL PROBABILITY PLOT OF BENZENE IN ACTIVATED SLUDGE PLANT EFFLUENT AT ESSO REFINERY

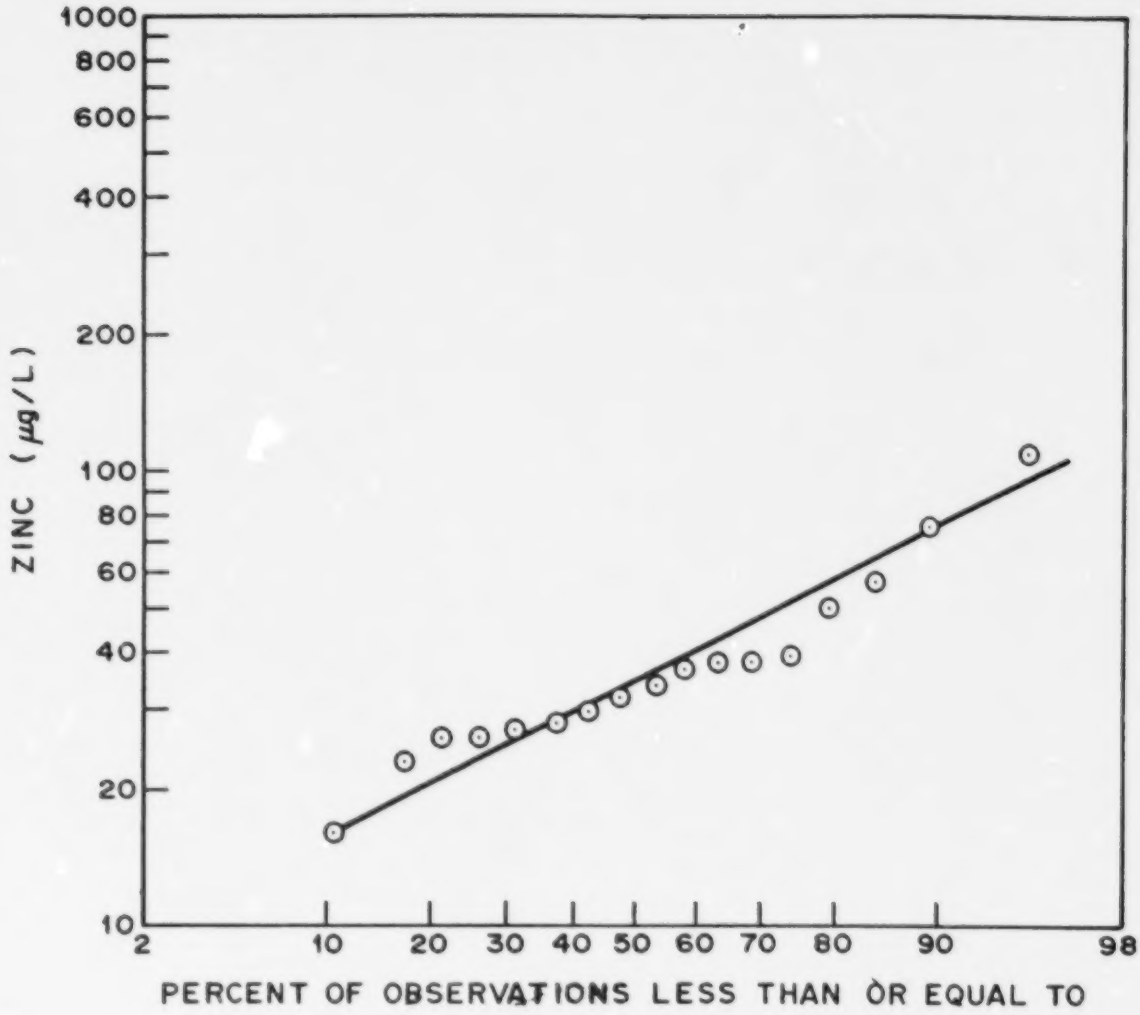

FIGURE E-3 LOG NORMAL PROBABILITY PLOT OF ZINC IN ACTIVATED SLUDGE PLANT EFFLUENT AT ESSO REFINERY

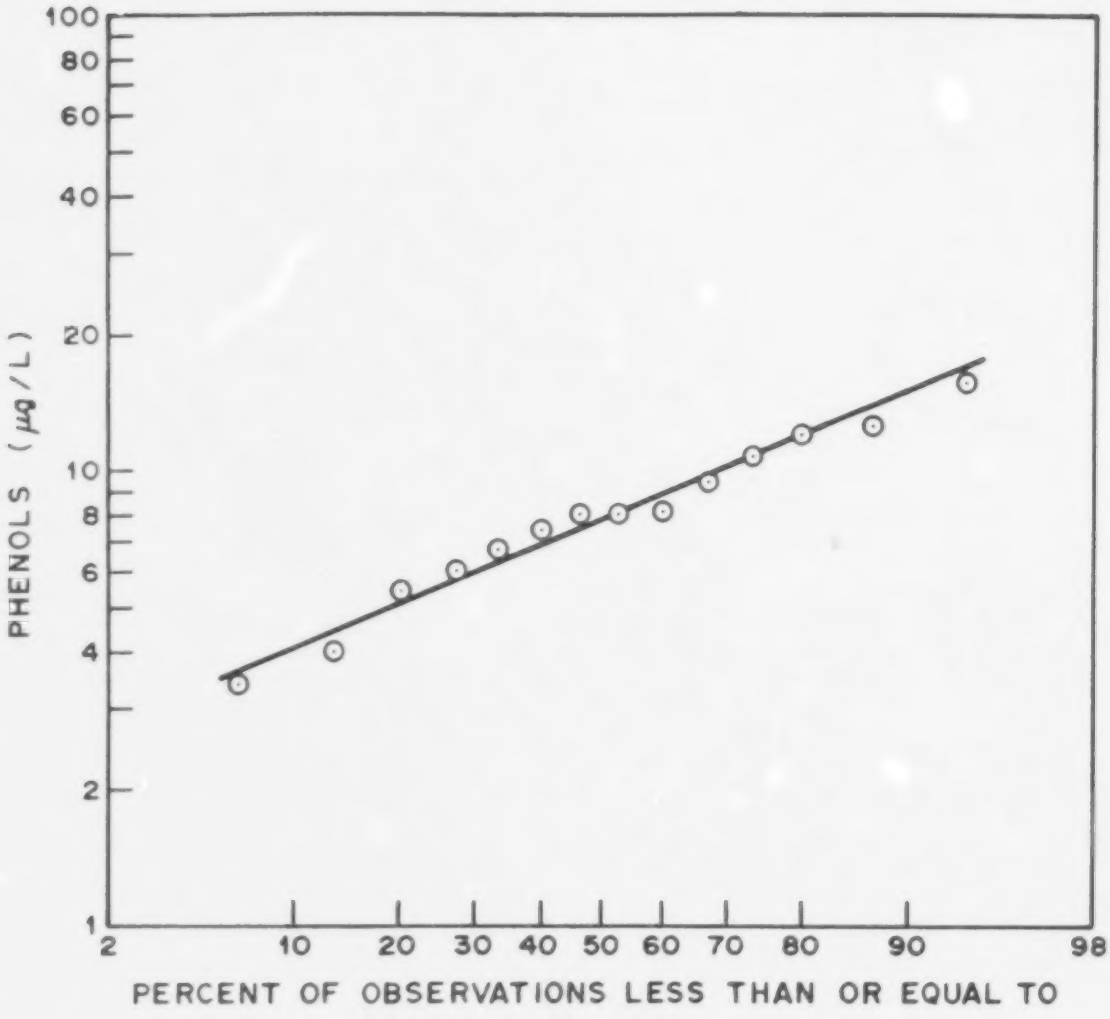

FIGURE E-4 LOG NORMAL PROBABILITY PLOT OF PHENOLS IN ACTIVATED SLUDGE PLANT EFFLUENT AT ESSO REFINERY

APPENDIX F

QA/QC PROGRAM RESULTS

APPENDIX F - QA/QC PROGRAM RESULTS

F-1 Conventional Contaminants and Metals

Field duplicate and field blank results from the conventional parameters analysis are presented in Table F-1. It can be noted from this table that there was good reproducibility in laboratory and field methods, shown from the field duplicate results. With the exception of oil and grease, there was no evidence of contamination in field blank samples.

Oil and grease at low levels (4-10 mg/L) was found in the field blank, a laboratory blank and a subsequent field blank for a similar study being conducted simultaneous with this monitoring program. Since there is no source of oil or grease in the still that could enter the distilled water, and sample bottles (if contamination is the question) were not in contact with the laboratory blank, it was concluded that a consistent laboratory error was occurring. One possible cause of error was that the volume of sample used was insufficient to provide precision at low levels. However, since all method and field blank analyses results in a positive error, it was more likely that a laboratory method error was occurring.

F-2 Trace Organics

Field duplicate and field blank results from the analyses of trace organics are presented in Table F-2. As indicated by the field duplicate results for volatile aromatic hydrocarbons and base neutral extractable organics, good reproducibility existed in both field and laboratory methods.

Low levels of volatile organics (benzene, ethylbenzene and xylenes) were found in the field blank taken during the second sampling period at Esso Refinery. Although concentrations were less than 4 ug/L, these levels were of similar magnitude to the concentrations of these compounds found for the Esso Refinery activated sludge plant effluent.

Phthalate esters were the only base neutral extractable organics detected in field blank samples at both plants. It should be noted that the presence of phthalate esters, which are common plasticizers, were probably a result of contamination from the various plastic materials used in the field (i.e. plastic distilled water container, plastic gloves, etc.).

TABLE F-1: QA/QC RESULTS FOR CONVENTIONAL CONTAMINANTS AND METALS

	FIELD DUPLICATE SAMPLES						FIELD BLANK SAMPLES			
	ESSO REFINERY				PETRO-CANADA REFINERY					
	Aug 11 - 22		Sep 15 - 26		Sep 16 - 27		ESSO REFINERY		PETRO-CANADA REFINERY	
	SAMPLE	DUPLICATE	SAMPLE	DUPLICATE	SAMPLE	DUPLICATE	Aug 11 - 22	Sep 15 - 26	Sep 16 - 29	
Conventional										
Alkalinity (mg/L as $CaCO_3$)	14	14	75	76	164	158	2	2	2	
Suspended Solids (mg/L)	NA	NA	70	70	50	60	<1	<1	<1	
DOC (mg/L)	NA	NA	11.8	11.3	19.5	19.1	<0.004	<0.004	<0.004	
TKN (mg/L)	3.04	2.27	2.4	2.3	NA	NA	<1.0	<1.0	<1.0	
NH_3-N (mg/L)	<1.0	<1.0	<1.0	<1.0	20.6	20.0	<1.0	<1.0	<1.0	
NO_3-N (mg/L)	7.6	7.2	0.49	0.49	2.1	2.2	0.21	<0.01	<0.01	
NO_2-N (mg/L)	0.014	0.014	<0.01	0.01	0.13	0.13	<0.01	<0.01	<0.01	
Total Phenols (ug/L)	9.4	9.4	104.9	104.9	18,000	19,300	5.4	2.6	<1	
Phosphorus (mg/L)	-	-	0.65	0.65	<0.13	<0.13	<0.13	<0.11	<0.10	DET.
Oil and Grease (mg/L)	6	7	6	4	17	19	5	4	5	LIMIT
Metals (ug/L)										
As	5	5	4	4	31	31	ND	ND	ND	1
Cd	ND	ND	ND	ND	ND	ND	ND	ND	ND	1
Cr	2	3	4	6	300	300	ND	ND	ND	1
Cu	9	8	14	20	6	5	2	ND	ND	1
Fe	160	170	1,550	1,570	1,030	1,070	ND	ND	ND	30
Pb	1	2	9	10	13	14	ND	ND	ND	1
Hg	0.05	0.05	ND	ND	ND	ND	ND	ND	ND	0.05
Ni	6	5	5	7	5	6	ND	ND	ND	1
Zn	25	27	70	78	110	120	ND	ND	ND	10

NA = Field duplicates were not analyzed for any samples

TABLE F-2: QA/QC RESULTS FOR VOLATILE AROMATIC COMPOUNDS AND BASE NEUTRAL EXTRACTABLE ORGANIC COMPOUNDS

	FIELD DUPLICATE SAMPLES						FIELD BLANK SAMPLES			
	ESSO REFINERY				PETRO CANADA REFINERY					
	Aug 11 - 22		Sep 15 - 26		Sep 16 - 27		ESSO REFINERY		PETRO-CANADA REFINERY	DET.
	SAMPLE	DUPLICATE	SAMPLE	DUPLICATE	SAMPLE	DUPLICATE	Aug 11 - 22	Sep 15 - 26	Sep 16 - 29	LIMIT
Volatile Aromatic Hydrocarbons (ug/L)										
Benzene	ND	ND	314	300	958	823	ND	1.6	ND	1.0
Ethylbenzene	ND	ND	192	182	718	677	ND	2.7	ND	1.0
Toluene	ND	ND	21	13	89	73	ND	ND	ND	1.0
Xylenes	ND	ND	500	541	690	560	ND	3.7	ND	1.0
Base Neutral Extractables (ug/L)										
Acenaphthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Acenaphthylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.5
Anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Methyl Anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
bis (2-chloroethyxyl) methane	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.3
bis (2-chloroethyl) ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.7
bis (2-chloroisopropyl) ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.7
bis (2-ethylhexyl)phthalate	3.2	3.2	30	39	29.4	27.5	3.6	61	9.2	2.5
Benzidine	ND	ND	ND	ND	ND	ND	ND	ND	ND	44
Benzo(a)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.8
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Benzo(b)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.8
Benzo(g,h,i)perylene	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.1
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Butyl Benzylphthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Chrysene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Di-n-butylphthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Di-n-octylphthalate	ND	ND	ND	ND	ND	ND	22.3	ND	ND	2.5
Dibenzo(a,h)anthracene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.5
Diethylphthalate	ND	ND	ND	ND	ND	ND	3.1	ND	ND	2.5
Dimethylphthalate	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.6
Fluoranthene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.2
Fluorene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Hexachlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Hexachlorobutadiene	ND	ND	ND	ND	ND	ND	ND	ND	ND	.9
Hexachloroethane	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.6
Indeno(1,2-c,d)pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.7
Isophorone	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.2
N-nitrosodiphenylamine	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.6
Methyl Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Dimethyl Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Trimethyl Naphthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.0
Nitrobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
Phenanthrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.4
Pyrene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
1,2,4-Trichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
1,2-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
1,3-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
1,4-Dichlorobenzene	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.4
2,4-Dinitrotoluene	ND	ND	ND	ND	ND	ND	ND	ND	ND	5.7
2,6-Dinitrotoluene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
2-chloronephthalene	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
3,3'-Dichlorobenzidine	ND	ND	ND	ND	ND	ND	ND	ND	ND	16.5
4-Bromophenyl phenyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.9
4-chlorophenyl phenyl ether	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.2

Samples were spiked with surrogate standard compounds for GC/MS analyses. Table F-3 presents the recommended surrogate compound recovery ranges and those achieved during sample analysis. In most cases, the recoveries were within the ranges recommended by the EPA[6]. The exceptions were not considered significant in that they were only marginally outside of the recommended ranges. Recoveries averaged from 95 to 100 percent for volatile organic compound surrogate standards and from 82 to 87 percent for the base neutral extractable organic compound surrogate standards.

F-3 MOE Results

F-3.1 MOE Audit Sample Results Review

As a part of the design of the study, a duplicate 24-hr composite sample was taken by CANVIRO at each of the two refineries of the biological treatment plant effluent stream. These duplicate samples were submitted to and analyzed by Ontario Ministry of the Environment, Laboratory Services Branch, Rexdale, Ontario (MOE).

All analyses for target compounds were carried out using standard methods in use at the Laboratory as defined in Handbook of Analytical Methods for Environmental Samples (HAMES), Ministry of the Environment, 1979. The only alternates employed were in the area of acid/base/neutrals and volatiles analysis where HRGC/MS (Hewlett Packard MSD) was the instrumentation with sample preparation by in-situ acetylation and extraction for acid/base neutrals and sample introduction by purge and trap (Tekmar LSC II) for volatiles. Acid/base/neutrals were identified and quantified in Selected Ion Monitoring (SIM) mode using 3 ions (1 major ion used for quantitation, 2 other ions used as qualifiers), while volatiles were identified and quantified in full scan mode again using 3 ions.

The results of the MOE analyses are presented with the corresponding CAN TEST analyses in Table F-4. Also presented are the MOE results for field blanks provided by CANVIRO (MOE sample containers shipped to the field, filled with distilled water in use by sampling crews, returned to MOE for analysis).

TABLE F-3: TRACE ORGANIC SURROGATE COMPOUND RECOVERIES
(EXPRESSED AS % RECOVERY)

SAMPLE	SAMPLE TYPE	SPIKED SURROGATE VOLATILE COMPOUND		SPIKED SURROGATE BASE NEUTRAL COMPOUND		
		Toluene-d8	1,2-Dichloro-ethane-d4	Chrysene-d12	Naphthalene-d8	Penanthrene-d10
RECOVERY RANGE		**88 - 110%**	**76 - 114%**	**40 - 130%**	**35 - 119%**	**65 - 128%**
LEVEL OF SPIKE		10 - 50 ug/mL		25 ug/mL	25 ug/mL	25 ug/mL
ESSO REFINERY						
11/8 - AM	E	100%	103%	72%	96%	79%
11/8 - PM	E	91	112	74	105	85
13/8 - AM	E	99	102	70	100	93
13/8 - PM	E	100	100	78	97	92
15/8 - AM	E	106	92	44	81	81
15/8 - PM	E	104	100	100	105	95
17/8 - AM	E	101	94	81	106	87
17/8 - PM	E	110	102	86	121	81
19/8 - AM	E	104	103	72	82	110
19/8 - PM	E-Dup.	99	107	64	88	121
21/8 - AM	E	109	96	53	93	110
21/8 - PM	E-Dup.	101	87	50	88	101
21/8	F.B.	109	96	109	79	88
15/9	I	107	97	74	81	110
15/9	E	105	87	76	72	74
15/9	E-Dup.	102	88	114	73	92
17/9	I	104	91	54	78	98
17/9	E	98	103	73	92	116
19/9	I	101	92	110	86	70
19/9	E	104	98	114	60	100
21/9	I	108	95	110	82	68
21/9	E	102	92	61	82	70
23/9	I	83	98	74	72	65
23/9	E	89	91	110	117	120
25/9	I	109	105	87	80	68
25/9	E	109	100	110	70	72
25/9	F.B.	89	93	50	88	94
Petro-Canada Refinery						
16/9	I	105	102	83	89	93
16/9	E	102	92	110	110	68
18/9	I	102	106	100	110	96
18/9	E	90	109	83	80	67
20/9	I	101	106	84	82	64
20/9	E	107	100	60	86	74
22/9	I	103	97	60	55	60
22/9	E	101	93	110	74	70
24/9	I	107	98	110	60	77
24/9	I-Dup.	110	91	79	78	114
24/9	E	102	97	67	84	112
26/9	I	104	96	54	78	70
26/9	E	110	95	110	77	68
26/9	F.B.	97	89	77	110	110
AVERAGE		100	95	82	87	87
RANGE		83 - 110	88 - 112	44 - 114	55 - 121	64 - 121

I = Influent Sample
E = Effluent Sample
Dup = Duplicate Sample
F.B. = Field Blank

TABLE F-4: COMPARISON OF MOE AND CANVIRO ANALYTICAL DATA FOR ACTIVATED SLUDGE PLANT EFFLUENTS FROM ESSO REFINERY AND PETRO-CANADA REFINERY

PARAMETER	ESSO REFINERY (19 AUGUST)			PETRO-CANADA REFINERY (18 SEPT)	
	CANVIRO	MOE	FIELD BLANK	CANVIRO	MOE
Conventional Contaminants					
pH	6.9	7.35	8	7.2	7.43
Conductivity (umhos/cm)	910	1,019	5.0	1,200	1,197
Suspended Solids (mg/L)	6	6.6	<0.6	80	67.4
Dissolved Organic Carbon (mg/L)	12.2	6.8	<0.4	16.0	14.4
Total Kjeldahl Nitrogen (mg/L)	2.01	1.2	<0.2	19.4	19.8
Ammonia Nitrogen (mg/L)	<1.0	<0.15	<0.1	14.8	14.9
Nitrate Nitrogen (mg/L)	6.8	6.65	<0.05	0.26	<0.05
Nitrite Nitrogen (mg/L)	0.011	MD	<0.005	<0.01	<0.015
Phenols (ug/L)	12.0	12	5.8	40.4	38
Oil and Grease (mg/L)	7	28	19	12	4
Metals (ug/L)					
Arsenic	4	<100	<100	27	NM
Cadmium	2	<6	<6	<1	<10
Chromium	1	<20	<20	31	290
Copper	10	<20	<20	12	<100
Iron	190	<60	<60	1,550	1,900
Lead	1	<60	<60	19	<100
Mercury	<0.05	NM	NM	0.20	NA
Nickel	8	<20	<20	16	<100
Zinc	66	<40	<40	170	150
Volatile Organic Compounds (ug/L)					
Benzene	2.3	<1	<1	<1	<1
Ethylbenzene	<1	<1	<1	<1	<1
Toluene	<1	<1	<1	<1	<1
Xylenes	1.4	<1	<1	<1	<1
1,2-Dichloroethane	<1	<1	<1	<2.8	5
1,2-Dichloropropane	<1	<1	<1	30	13
Methylene Chloride	NM	NM	NM	1.8	NM
Base Neutral Extractable Organics (ug/L)					
bis-(2-ethylhexyl)phthalate	3.2	30	TR <8	<2.5	TR <20
di-n-Butylphthalate	<2.5	33	<1	<2.5	<1

With the exceptions of conductivity, phenols and oil and grease, there was no evidence of contamination of field blank samples. Good to fair reproducibility was observed for most conventional contaminants (pH, conductivity, suspended solids, TKN, ammonia, nitrates, nitrites, and phenols). However, a discrepancy was noted in the oil and grease results. The field blank results for August at the Esso Refinery reported by MOE of 14 mg/L was significant given the effluent value of 28 mg/L. Since these values were much higher than those reported in the CANVIRO sample (7 mg/L), it was assumed there was a contamination problem with the field blank sample. The field blank for MOE was filled in the field while the CANVIRO field blank was filled in the CANVIRO lab in Kitchener. The results for the Petro-Canada survey (MOE 4 mg/L, CAN TEST 12 mg/L) indicated a discrepancy, the higher value reported by CANVIRO was expected as a result of the consistent method error discussed in Appendix F.

For metals analyzed by MOE, the ICP (simultaneous) and DCP (sequential) methods of analysis were applied in a characterization or forensic mode to determine the presence of a broad range of elements (49 in number, refer to Appendix Table F-5 for comprehensive list). As such, this method was less sensitive than that applied by CAN TEST. However, where data was reported by MOE above detection limits, there was good agreement with CAN TEST results. Two discrepancies were chromium at the Petro-Canada Refinery with MOE and CAN TEST reporting 290 and 31 ug/L, respectively, while at Esso, for lead, values of 80 and 198 ug/L were reported by MOE and CAN TEST. It must be noted that the MOE value for chromium on the Petro-Canada sample was analyzed by 3 separate methods - ICP sequential, ICP simultaneous and DCP sequential - with all three methods providing values between 270 and 298 ug/L.

Target volatile organic compound analyses performed by MOE showed no detectable levels (<1 ug/L) of the aromatic hydrocarbons benzene, ethylbenzene, toluene and xylene in the Esso sample, but levels of 3 ug/L for both benzene and xylenes at the Petro-Canada Refinery. CAN TEST results for the Esso Refinery showed low levels (<3 ug/L) on one sampling run but also similar levels in the August field blanks. 1,2-dichloropropane was also detected at the Petro-Canada site by both laboratories at a level of 30 and 13 ug/L for CAN TEST and MOE, respectively. 1,2-dichloroethane (5 ug/L), dichloromethane (7 ug/L), dichlorobromomethane (6 ug/L) and 1,2-dichloropropane (13

ug/L) were found only by MOE at the Petro-Canada Refinery. Although dichloromethane is a recognized laboratory contaminant for this analysis, no measurable level was observed in either the field or laboratory blanks.

It is noteworthy that both laboratories analyzed all samples based on a very comprehensive target list (EPA 624 or equivalent) and found no other detectable volatile organics in the final treated effluents based on these targets.

Acid/base neutral extractable target organics found by both laboratories included phthalic acid esters (bis-2-ethylhexyl and di-n-butyl phthalates specifically) at levels between detection (<1 ug/L) and 33 ug/L for all samples. The higher values of 30 and 33 ug/L reported by MOE on the Esso Refinery sample may be attributed to sample or laboratory contamination, especially with the known ubiquitous nature of these organics and their habit of cropping up in this analysis. Again it should be noted that both laboratories analyzed for a comprehensive list of target parameters and that very few compounds were observed based on these targets.

In summary, the results obtained from the two laboratories were in generally excellent agreement with each other on all but two or three compounds/tests (oil and grease, chromium and phthalates). The organics findings in particular were good and supportive of previous and historic findings.

F-3.2 Characterization of Forensic Data Obtained by MOE

As a part of the MOE involvement in this project, the single effluent composites were subjected to a full scan volatile and base neutral extractable compound analysis. An inorganic scan of 49 elements was also undertaken using a combination of ICP and DCP. The comprehensive target list of compounds and elements involved in the full scan are listed in Table F-5.

A number of other compounds were observed and quantified above the 1 ug/L level for the GC/MS analyses, or above the method detection limits for the elemental scan. The actual identifications and results are presented in Tables F-6 and F-7.

TABLE F-5: COMPREHENSIVE TARGET LIST FOR MOE SCAN

METALS		DET.LIMIT (mg/L)
Copper	†	0.02
Nickel	†	0.02
Zinc	†	0.04
Cadmium	†	0.006
Cobalt	†	0.02
Chromium	†	0.02
Lead	†	0.06
Iron	†	0.06
Manganese	†	0.02
Aluminum	†	0.06
Calcium	†	0.5
Magnesium	†	0.5
Sodium	†	1
Potassium	†	1
Vanadium	†	0.02
Molybdenum	†	0.02
Barium	†	0.02
Beryllium	†	0.02
Strontium	†	0.02
Titanium	†	0.02
Silver	†	0.1
Arsenic	†	0.1
Boron	†	0.2
Phosphorus	†	0.4
Sulphur	†	0.2
Gold	*	0.1
Bismuth	*	1
Cerium	*	0.1
Cesium	*	5
Gallium	*	1
Germanium	*	0.1
Mercury	*	5
Indium	*	0.2
Lanthaniu	*	0.1
Lithium	*	1
Neodymium	*	0.1
Platinum	*	1
Rhodium	*	0.1
Antimony	*	5
Scandium	*	1
Selenium	*	5
Silicon	*	0.5
Samarium	*	0.1
Tin	*	1
Thallium	*	1
Uranium	*	5
Tungsten	*	1
Yttrium	*	0.1
Thorium	*	5

VOLATILE ORGANIC COMPOUNDS	DET.LIMIT (ug/L)
1,1-Dichloroethylene	1
Dichloromethane	1
t-1,2-Dichloroethylene	1
1,1-Dichloroethane	1
Chloroform	1
1,1,1-Trichloroethane	1
1,2-Dichloroethane	1
Carbontetrachloride	1
Benzene	1
1,2-Dichloropropane	1
Trichloroethylene	1
Bromodichloromethane	1
Toluene	1
1,1,2-Trichloroethane	1
Chlorodibromomethane	1
Tetrachloroethylene	1
Chlorobenzene	1
Ethylbenzene	1
m- + p-xylenes	1
Bromoform	1
o-xylene	1
1,1,2,2-Tetrachloroethane	1
1,4-Dichlorobenzene	1
1,3-Dichlorobenzene	1
1,2-Dichlorobenzene	1
Hexachloroethane	1
1,3,5-Trichlorobenzene	2
1,2,4-Trichlorobenzene	2
Hexachloro(1,3)butadiene	1
1,2,3-Trichlorobenzene	2
2,4,5-Trichlorotoluene	1
2,3,6-Trichlorotoluene	1
1,2,3,5-Tetrachlorobenzene	1
1,2,4,5-Tetrachlorobenzene	1
A,2,6-Trichlorotoluene	1
1,2,3,4-Tetrachlorobenzene	1
Pentachlorobenzene	1
PCB (total)	20
Hexachlorobenzene	1
Heptachlor	1
Aldrin	1
p,p'-DDE	1
Mirex	5
a-HCH	1
b-HCH	1
Lindane	1
a-Chlordane	2
g-Chlordane	2
oxyChlordane	2
o,p'-DDT	5
p,p'-DDD	5
p,p'-DDT	5
Methoxychlor	5
Heptachlor Epoxide	1
Endosulfan I	2
Endosulfan II	5
Endosulfan Sulphate	5
Octachlorostyrene	1

BASE NEUTRAL EXTRACTABLE ORGANIC COMPOUNDS	DET.LIMIT (ug/L)
Bis(2-chloroethyl)ether	5
Bis(2-chloroisopropyl)ether	5
Nitrobenzene	5
Bis(2-chloroethoxy)methane	1
Naphthalene	1
1-Methylnaphthalene	1
Dimethylphthalate	1
Acenaphthylene	1
2,6-Dinitrotoluene	2
Acenaphthene	1
4-Chlorophenylphenylether	5
2,4-Dinitrotoluene	2
Diethylphthalate	1
2-Chloroethylvinylether	2
Fluorene	1
n-Nitrosodiphenylamine	2
4-Bromophenylphenylether	1
Phenanthrene	1
Anthracene	1
Di-isobutylphthalate	1
Di-n-butylphthalate	1
Fluoranthene	1
Pyrene	1
Butylbenzylphthalate	5
Benzo(a)anthracene	1
Chrysene	1
Bis-2-ethylhexylphthalate	5
Di-n-octylphthalate	1
Benzo(k)fluoranthene	1
Benzo(b)fluoranthene	1
Benzo(a)pyrene	1
Indeno(1,2,3-c,d)pyrene	1
Dibenzo(a,h)anthracene	2
Benzo(g,h,i)perylene	1

ACID EXTRACTABLE COMPOUNDS	DET.LIMIT (ug/L)
Phenol (Gas Chromatog)	2
2,4-Dimethylphenol	5
p-Chloro-m-cresol	1
2,3-Dichlorophenol	1
2,4-Dichlorophenol	1
2-Nitrophenol	5
2,4,6-Trichlorophenol	1
4-Nitrophenol	6
2,3,4,5-Tetrachlorophenol	1
2,3,4,6-Tetrachlorophenol	2
2,4-Dinitrophenol	Unavail
4,6-Dinitro-o-cresol	Unavail
Pentachlorophenol	1

† Analyses performed by ICP.
* Analysis performed by DCP.

TABLE F-6: ADDITIONAL TRACE ORGANIC COMPOUNDS DETECTED (>1 ug/L) IN MOE ANALYSIS

COMPOUND IDENTIFIED	APPROXIMATE CONCENTRATION (ug/L)
Petro-Canada	
Methyldecahydronaphthalene	30
Dimethyldecahydronaphthalene	30
Trimethyldecahydronaphthalene	60
Methylbiphenyl	400
Dimethylbiphenyl	200
Xanthene-9-one	6
Trimethylbenzoic Acid	9
Esso Canada	
Atrazine	7
Ethyl pyrrole-2,5-dione	3
Piperidine (C3 alkyl)	1
3-(1-methyl-2-pyrrolidinyl) pyridine	2
5-Methoxy-2-methyl-indole	9
3-Methyl indole-4-ol	9
Methylsulfinylbenzene	7
A polypropylene glycol	5
Tributyl phosphate	1
2-Butoxyethanol phosphate	4
1,1-Oxybis(2-ethoxy)ethane	4
Alkyl substituted 1-azabicyclo(2,2,2)octane	4

TABLE F-7: ADDITIONAL ELEMENTS DETECTED IN MOE ANALYSIS

ELEMENT IDENTIFIED	QUANTITATION (mg/L)
Esso Refinery	
Manganese	0.05
Aluminum	0.06
Calcium	37
Magnesium	8.90
Sodium	170
Potassium	3.5
Barium	0.03
Strontium	0.32
Phosphorus	0.60
Sulphur	29
Silicon	0.90

Analysis for these extractable compounds was performed on a Finnigan 4500 HRGC/MS using internal standard method and d10 anthracene for quantitation. The components isolated have only approximate concentrations indicated. This approximation is based on three major assumptions which are:

i) the extraction efficiency,
ii) the HRGC behaviour, and
iii) the MS response of the compound is identical to that of the internal standard added to every sample.

Compounds were identified from the NBS Library of Mass Spectra as supplied on the Finnigan/Incos data system (1984 edition). From the library search printout, the best match having purity, fit and reverse fit greater than 808 (maximum of 1000) was selected (i.e. 80% fit or greater). Identification also required the correct matching of retention time where available. All approximate concentrations reported have been rounded and reported to 1 significant figure.

These data are presented for review purposes only. Some of the compounds may be of concern and warrant further analysis and study (e.g. alkyl naphthalenes). None are currently on the Interim MOE or U.S. EPA Priority Pollutants lists so no attempt is made at assessing their environmental or health significance. It must be emphasized that this data is the result of a single analysis on one 24-hour composite sample so no statistical significance of presence or concentration is implied nor should be assumed.

The application of an elemental scan using a combination of ICP (simultaneous) and DCP (sequential) was only to the Esso Refinery sample due to a logistical problem at the MOE laboratory. As with the organic scan, few extra elements were observed above detection limits and most have been observed and reported in previous and historic documents.

The presence of the various salts (sodium, calcium, potassium) and sulphur is not unexpected given the use of brine solution at the refinery and the natural sulphur content of the crude oil.

APPENDIX G

ESSO REFINERY AND PETRO-CANADA REFINERY
OPERATIONAL PARAMATERS DURING STUDY PERIOD

TABLE G-1: ESSO REFINERY OPERATIONAL PARAMETERS DURING MONITORING PERIOD

DATE	CRUDE PROCESSING			RAINFALL (mm)	TREATING BALLAST/ STORM WATER	BIOX FLOW (1000 m^3/d)	REFINERY UPSETS, SHUT DOWNS ETC.
	VOLUME (1000 bbls/ day)	% LIGHT	% HEAVY				
11 Aug	NA	NA	NA	NA	yes	24.18	- No upsets reported by plant staff
12	NA	NA	NA	NA			
13	NA	NA	NA	NA	yes	24.36	
14	NA	NA	NA	NA			- Cleaning of clean water separator (sludge bottoms) 13 August
15	NA	NA	NA	NA	no	23.31	
16	NA	NA	NA	NA			
17	NA	NA	NA	NA	yes	21.20	
18	NA	NA	NA	NA			
19	NA	NA	NA	NA	no	23.81	
20	NA	NA	NA	NA			
21	NA	NA	NA	NA	yes	22.31	
15 Sept	119	87	13	34.6	yes	29.18	- No upsets reported by plant staff
16	118	89	11	0			
17	117	89	11	0	yes	19.65	
18	112	88	12	0.4			- Rainfall on 22 September caused exceptionally high flows to BIOX plant; some bypassed to river for a short period of time
19	92	88	12	5.0	yes	20.45	
20	93	86	14	TR			
21	94	85	15	0	no	18.32	
22	97	88	12	52.0			
23	107	91	9	6.8	yes	26.50	
24	108	91	9	0			
25	96	96	4	5.2	yes	26.54	
26	89	96	4	0			

NA = Information was not recorded

TABLE G-2: PETRO-CANADA REFINERY OPERATIONAL PARAMETERS DURING MONITORING PERIOD

DATE	CRUDE PROCESSING			RAINFALL (mm)	TREATING		BIOX FLOW (1000 m^3/d)	REFINERY UPSETS, SHUT DOWNS ETC.
	VOLUME (1000 bbls/ day)	% LIGHT	% HEAVY		BALLAST	STORM*		
16 Sept	60	55	45	20.5	yes	no	6.088	- Amine plant shut down for 4 hours on 16 16 September
17	60	55	45	0				
18	63	57	43	0	yes	no	6.091	
19	57	53	47	0				
20	57	53	47	2.0	no	no	4.594	- Refinery operation considered typical by plant staff
21	57	53	47	0				
22	57	53	47	0	no	no	4.133	
23	57	53	47	42.0				
24	57	53	47	5.9	no	no	4.925	
25	53	57	43	0				
26	53	57	43	5.4	no	no	3.974	
27	53	57	43	0				

* Stormwater that is normally collected in sheet drain system

APPENDIX H

ADDITIONAL VOLATILE ORGANIC COMPOUNDS QUALITATIVELY DETECTED IN ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT SAMPLES

TABLE H-1: NON-PRIORITY VOLATILE ORGANICS DETECTED IN ESSO, SARNIA ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT

COMPOUNDS	15 SEPT.		17 SEPT.		19 SEPT.		21 SEPT.		23 SEPT.		25 SEPT.	
	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.
Acetone	X		X		X		X		X		X	
Butane	X											
Cyclohexane							X		X			
Cyclopentane			X									
Dimethyldisulphide	X		X									
Demethylethylpentane	X											
Dimethyloctane			X									
Dimethylpentane									X		X	
Hexane	X				X		X					
2-Methylbutane	X											
Methyl cyclohexane	X		X				X				X	
Methylethylbenzene	X		X		X		X		X		X	
Methylethylcyclo-pentane	X											
Methylpentanol											X	
Methylpentanone	X		X									
2-Methyl-1-pentane	X		X									
Pentane	X								X			
Pentamethylheptane	X											
2-Propanol	X											
Propylheptanol	X											
Thiophene									X			
Trimethylbenzene			X				X		X			
Trimethyloctane									X		X	
Trimethylpentane	X		X									

TABLE H-2: NON-PRIORITY VOLATILE ORGANICS DETECTED IN PETRO TRAFALGAR ACTIVATED SLUDGE PLANT INFLUENT AND EFFLUENT

COMPOUNDS	16 SEPT.		18 SEPT.		20 SEPT.		22 SEPT.		24 SEPT.		26 SEPT.	
	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.	INF.	EFF.
Acetone	X		X		X		X		X		X	
Dibromoethane							X					
Dimethylpentane							X					
Hexane		X			X							
Methylcyclohexane	X				X						X	
Methylcyclopentane									X			
Methylethyl benzene	X		X		X		X					
Methylpentanol	X											
Methylpentene									X		X	
Methylthiophene					X		X					
Nonanol					X							
2-Propanol	X	X	X								X	
Trimethylbenzene	X		X		X		X		X			
Trimethyloctane					X		X					

APPENDIX I

MOE TOXICITY TEST RESULTS

APPENDIX I - MOE TOXICITY TEST RESULTS

I-1 Esso Refinery, Sarnia

Effluent samples from 22 August 1986 were tested for acute toxicity to rainbow trout according to the MOE bioassay protocol.

Table I-1 presents the mortality data for the 96-hour test. Table I-2 presents the pH and oxygen data for the tests. The results indicated the treated effluent from Esso Refinery CAS effluent to be non-acutely lethal to fish.

I-2 Petro-Canada Refinery, Trafalgar

Effluent samples from 16 September 1986 were tested for acute toxicity to rainbow trout according to the MOE bioassay protocol. Table I-3 presents the mortality data for the 96-hour test. Table I-4 presents the pH and oxygen data.

The 100 percent concentration, or the undiluted sample, caused lethality in the test fish where 60 percent mortality was observed. The surviving fish in this sample showed abnormal swimming behaviour (surfacing), an indication of stress from the exposure.

No mortalities were noted in any of the dilutions or in the control. The 96-hour LC50 was estimated to be equal to 95%. This result is questionable since no statistical confidence can be attached.

TABLE I-1: MORTALITY DATA FOR ESSO REFINERY ACTIVATED SLUDGE PLANT EFFLUENT TOXICITY TEST

NO. OF FISH IN TEST	TEST CONC'N (%)	MORTALITY AT ELAPSED TIME (hrs)												TOTAL MORTALITY (%)
		0.5	1.5	2	3	4	5	12	24	33	48	72	96	
10	100	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	65	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	40	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	30	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	20	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	10	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0
10	Control	0	0	0	0	NR	NR	NR	0	NR	0	0	0	0

NR = No Reading

* Average weight 1.1 g, average length 44 mm

96-Hour LC50 — 95% Confidence Limits: Upper — Lower

Non-Lethal

TABLE I-2: pH AND OXYGEN DATA FOR ESSO REFINERY ACTIVATED SLUDGE PLANT EFFLUENT TOXICITY TEST

TEST CONC'N (%)	STARTING pH	NO. OF FISH USED	VOL. OF TEST SOL'N (L)	FINAL DATA		
				TEMPERATURE (°C)	O_2 (mg/L)	pH
100	7.9	10	30	15	9.6	8.1
65	8.1	10	30	15	9.6	8.3
40	8.2	10	30	15	9.6	8.2
30	8.1	10	30	15	9.4	8.1
20	8.2	10	30	15	9.8	8.2
10	8.2	10	30	15	9.7	8.2
Control	7.7	10	30	15	9.5	7.9

TABLE I-3: MORTALITY DATA FOR PETRO-CANADA ACTIVATED SLUDGE PLANT EFFLUENT TOXICITY TEST

NO. OF FISH IN TEST*	TEST CONC'N (%)	MORTALITY AT ELAPSED TIME (hrs)												TOTAL MORTALITY (%)
		0.5	1.5	2	3	4	5	12	24	33	48	72	96	
10	100	0	0	0	0	0	0	NR	0	NR	0	0	6	60
10	65	0	0	0	0	0	0	NR	0	NR	0	0	0	0
10	40	0	0	0	0	0	0	NR	0	NR	0	0	0	0
10	30	0	0	0	0	0	0	NR	0	NR	0	0	0	0
10	20	0	0	0	0	0	0	NR	0	NR	0	0	0	0
10	10	0	0	0	0	0	0	NR	0	NR	0	0	0	0
10	Control	0	0	0	0	0	0	NR	0	NR	0	0	0	0

NR = No Reading

* Average weight 1.4 g, average length 46 mm

96-Hour LC50	95% Confidence Limits Upper	Lower
@ 95%	Unreliable	

TABLE I-4: pH AND OXYGEN DATA FOR PETRO-CANADA ACTIVATED SLUDGE PLANT EFFLUENT TOXICITY TEST

TEST CONC'N (%)	STARTING pH	NO. OF FISH USED	VOL. OF TEST SOL'N (L)	FINAL DATA		
				TEMPERATURE (°C)	O_2 (mg/L)	pH
100	7.6	10	30	15	9.4	8.2
65	8.0	10	30	15	10.2	8.0
40	8.2	10	30	15	10.4	8.2
30	8.2	10	30	15	10.4	8.2
20	8.2	10	30	15	10.3	8.2
10	8.2	10	30	15	10.1	8.2
Control	8.1	10	30	15	10.0	8.1